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THE MEMPHIS DEPOT
TENNESSEE

ADMINISTRATIVE RECORD
COVER SHEET

AR File Number 877

Part III of III

1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8081A is applied to the analysis of organochlorine pesticides by GC/ECD. This Appendix may also to be applied when discontinued SW-846 Method 8080A is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL North Canton sample extraction SOPs. (CORP-OP-0001NC)

Table B-1 lists compounds, which are routinely determined by this method, and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

At client request, this method may also be used for the analysis of PCBs (Arochlors) in combination with pesticides, although these are normally analyzed following method 8082, as described in Appendix C of this SOP. In any event, if samples for PCB analysis do not need the acid clean up procedure, then the same injection may be used for method 8081B and 8082, assuming all calibration and QC requirements for both methods are met. Extracts that have been acid cleaned may not be analyzed for pesticides, since several of the pesticides will be degraded.

1.1. The associated LIMS method code is QJ (8081A).

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of organochlorine pesticides. The pesticides are injected onto the column and separated and detected by electron capture detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Avoiding contact with any plastic materials minimizes interferences from phthalates.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001NC.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001NC. Using hexane / acetone as the extraction solvent (rather than hexane / methylene chloride) will reduce the amount of interferences extracted.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, and the BHCs. Primary standards of these toxic compounds should be prepared in a hood.

5.4. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.5. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table B-2 for analytical columns

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Refer to Table B-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Refer to tables B-5 and B-6 for details of surrogate standards

7.4. Column Degradation Evaluation Mix

A mid-level standard containing 4,4'-DDT and Endrin and not containing any of their breakdown products must be prepared for evaluation of degradation of these compounds by the GC column and injection port. This mix must be replaced after one year, or whenever corrective action to columns fails to eliminate the breakdown of the compounds, whichever is shorter. This solution also contains the surrogates. Refer to Table B-4 for details of the column degradation evaluation mix.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Refer to Table B-2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both columns. Closely eluting pairs are DDE and Dieldrin on the Rtx-5 or DB-5 column and Endosulfan II and DDD on the 1701 column.

10.3. Column Degradation Evaluation

Before any calibration runs, either initial or 12 hour, The column evaluation mix must be injected before each initial or daily calibration. The degradation of DDT and endrin must be calculated (see equations 9 and 10) and each shown to be less than 15% before calibration can proceed. This is only necessary if the target compound list includes DDT, Endrin, or any of their degradation products.

If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:

- Replacement of the injection port liner or the glass wool.
- Cutting off a portion of the injection end of a capillary column.
- Replacing the GC column.

10.4. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.4.1. Refer to Table B-7 for the initial calibration analytical sequence.

10.4.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4.3 The surrogate calibration curve is calculated from the Individual AB mix. Surrogates in the other calibration standards are used only as retention time markers. If there are resolution problems, then the A and B mixes may be analyzed separately.

10.4.4. For multi-component pesticides:

Single point calibration is used for multi-component pesticides (typically toxaphene and technical chlordane). Two options are possible; the same quantitation option must be used for standards and samples. Refer to section 12.3 for guidance on which option to use.

10.4.5. For multi-component analytes, the mid level standard must be analyzed as part of the initial calibration. This single point calibration is used to quantitate multi-component analytes.

10.4.6. The analyst may include a full 5 point calibration for any of the multi-component analytes with the initial calibration.

10.5. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

10.5.1. At a minimum, the 12 hour calibration includes analysis of the breakdown mix followed by mid level standards of any single and multi-component analytes.

10.5.2. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.6. Continuing Calibration

The AB calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. The continuing calibration standard need not include multi-component analytes. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.6.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001NC.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001NC.

11.4. Suggested gas chromatographic conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-7.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. Identification of Multi-component Analytes

Retention time windows are also used for identification of multi-component analytes, but the "fingerprint" produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.3. Quantitation of Multi-component Analytes

Use 3-10 major peaks or total area for quantitation as described in section 10.4.4, initial calibration of multi-component analytes.

12.3.1 If there are no interfering peaks within the envelope of the multi-component analyte, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

12.3.1.1 Multiple peak option

This option is particularly valuable if toxaphene is identified but interferences make quantitation based on total area difficult. Select 3-10 major peaks in the analyte pattern Calculate the response using the total area or total height of these peaks Alternatively, find the response of each of the 3-10 peaks per multi-peak pesticide, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be

coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

Chlordane may be quantitated either using the multiple peak option (12.3.1.1) total area option (12.3.1 2) or by quantitation of the major components, α-chlordane, γ-chlordane and heptachlor.

12.3.1.2. Total area option

The total area of the standards and samples may be used for quantitation of multi-component analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multi-component pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

12.4. Second column confirmation multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

12.5. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX). Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

12.6. Calculation of Column Degradation/% Breakdown (%B)

Equation 9

$$DDT\ \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} \times 100$$

where:
A_{DDD}, A_{DDE}, and A_{DDT} = the response of the peaks for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in the column degradation evaluation mix.

Equation 10

$$Endrin\ \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} \times 100$$

where:
A_{EK}, A_{EA}, and A_E = the response of endrin ketone, endrin aldehyde, and endrin in the column degradation evaluation mix.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP. Example performance limits are listed in Table B-8. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Update III, December 1996, Method 8081A

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2 Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aldrin	0 05	1.7	50
α-BHC	0.05	1.7	50
β-BHC	0.05	1.7	50
δ-BHC	0.05	1.7	50
γ-BHC (Lindane)	0.05	1.7	50
α-Chlordane	0.05	1.7	50
γ-Chlordane	0.05	1.7	50
Chlordane (technical)	0.5	17	500
4,4'-DDD	0.05	1.7	50
4,4'-DDE	0.05	1.7	50
4,4'-DDT	0.05	1.7	50
Dieldrin	0.05	1.7	50
Endosulfan I	0.05	1.7	50
Endosulfan II	0.05	1.7	50
Endosulfan Sulfate	0.05	1.7	50
Endrin	0.05	1 7	50
Endrin Aldehyde	0.05	1.7	50
Heptachlor	0.05	1.7	50
Heptachlor Epoxide	0.05	1.7	50
Methoxychlor	0.1	3 3	100
Toxaphene	2.0	67	2000
APPENDIX IX ADD ONs			
Diallate	1.0	33	1000
Isodrin	0.1	3.3	100
Chlorobenzilate	0.1	3.3	100
Kepone[1]	1.0	33	1000

[1] Kepone is sometimes requested for analysis by method 8081A. However kepone may produce peaks with broad tails that elute later than the standard by up to a minute (presumably due to hemi-acetal formation). As a result kepone analysis by 8081A is unreliable and not recommended. Analysis by method 8270C is a possible alternative. Note: alpha chlordane, gamma chlordane, and endrin ketone are not required for some projects.

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol		Final Vol
Ground water	1000 mL	10 mL	
Low-level Soil	30 g		10 mL
High-level soil / waste	1 g		10 mL

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Table B-2	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	120°C for 1 min, 8 5°C/min to 285°C, , 6 min hold
Column 1	Rtx-CLPesticides 30m x 0.32mm id, 0.5µm
Column 2	Rtx-35 30m x 0.32 mm id, 0.5µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table B-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[2]
Individual Mix AB[1]						
Aldrin	5	10	25	50	100	200
g-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	25	50	100	200
Methoxychlor	10	20	50	100	200	400
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4'-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
Endrin Ketone	5	10	25	50	100	200
β-BHC	5	10	25	50	100	200
δ-BHC	5	10	25	50	100	200
α-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4,4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
α-Chlordane[3]	5	10	25	50	100	200
γ-Chlordane[3]	5	10	25	50	100	200
Multi-component Standards						
Chlordane (Technical)			250[4]			
Toxaphene			1000[5]			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Standards may be split into an A and B mix if resolution of all compounds on both columns is not obtained.

[2] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.

[3] Compounds may be used in lieu of running a daily technical Chlordane standard for samples that are non-detect for technical Chlordane.

[4] This standard may be used for quantitation of technical chlordane between 50 and 1000 ng/mL. If the chlordane is more concentrated, the extract must be diluted and reanalyzed.

[5] This standard may be used for quantitation of toxaphene between 200 and 4000 ng/mL. If the toxaphene is more concentrated, the extract must be diluted and reanalyzed.

Table B-4	
Column Degradation Evaluation Mix ng/mL	
Component	Concentration
4,4'-DDT	25
Endrin	25
Tetrachloro-m-xylene (Surrogate)	20
Decachlorobiphenyl (Surrogate)	20

Table B-5			
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg			
	Aqueous	Soil	Waste
gamma BHC (Lindane)	0.20	33.3	200
Aldrin	0.20	33.3	200
Heptachlor	0.20	33 3	200
Dieldrin	0.50	33.3	500
Endrin	0.50	33.3	500
4,4'DDT	0.50	33.3	500
Tetrachloro-m-xylene (Surrogate)	0.20	33.3	200
Decachlorobiphenyl (Surrogate)	0.20	33.3	200

Table B-6		
LCS/Matrix Spike and Surrogate Spike levels for TCLP µg/L or µg/kg		
	Aqueous	Waste
Heptachlor	5	500
Heptachlor epoxide	5	500
Lindane	5	500
Endrin	5	500
Methoxychlor	10	1000

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)	
Breakdown Mix	
Individual mix AB	All levels
Technical Chlordane	Level 3[1]
Toxaphene	Level 3[1]
Up to 20 samples unless 12 hours comes first)	
Solvent blank (optional)	
Individual mix AB	Mid level (Continuing calibration)
Samples	
After 12 hours·	
Breakdown mix	
Individual mix AB	
Any other single component analytes	
Any multi-component analytes	

[1] A five point curve for any of the multi-component analytes may be included
If Arochlors are included, a 5 point calibration for Arochlor 1016/1260 should be included with the initial calibration and a single point for the other Arochlors. The mid point 1016/1260 mix is included with the daily calibration (every 12 hours).

Note: A solvent blank or primer may be analyzed at any time during the sequence when highly contaminated samples are expected. A solvent blank or primer may not be analyzed as routine immediately prior to standards.

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix AB, and the breakdown mix must be run before the continuing calibration

Table B-8

Example Performance limits, four replicate initial demonstration of capability

Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
Aldrin	46-112	21
alpha-BHC	51-122	24
beta-BHC	61-120	32
delta-BHC	49.5-118.5	36
gamma-BHC	57-116	23
Chlordane	44.8-108.6	20
4,4'-DDD	52-126	28
4,4'-DDE	46-120	27.5
4,4'-DDT	54-137	36
Dieldrin	42.5-124.5	38
Endosulfan I	43-141	24 5
Endosulfan II	78-171	61
Endosulfan Sulfate	62-132	27
Endrin	49-126	37
Heptachlor	57-100	20
Heptachlor Epoxide	43.5-131 5	25.4
Toxaphene	44.4-111 2	20

1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polychlorinated biphenyls (PCB) by GC/ECD. This Appendix is to be applied when SW-846 Method 8082 is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (CORP-OP-0001NC). The PCBs are determined and quantitated as Arochlor mixes.

1.2. Table C-1 lists compounds, which are routinely determined by this method, and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

Note: SW-846 method 8082 provides incomplete guidance for determination of individual PCB congeners. This SOP does not include directions for congener specific analysis.

1.3. The associated LIMS method code is QH (8082).

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of PCBs. The PCBs are injected onto the column and separated and detected by electron capture detection. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Avoiding contact with any plastic materials minimizes interferences from phthalates.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001NC.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001NC.

5. SAFETY

5.1 Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.4. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table C-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem

7.2. Refer to Table C-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Other surrogates may be used at client request. Refer to Table C-4 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Initial Calibration

10.2.1. Refer to Table C-5 for the initial calibration analytical sequence

10.2.2. The response for each Arochlor will be calculated by the procedures described in the general method for GC analysis, with the following modifications.

10.2.3. A five point calibration of the Arochlor 1016/1260 mix is generated with at least mid level single points for the other Aroclor mixes. The average response factor is used to quantitate Arochlors 1260 and 1016, other Arochlors are quantitated from the mid level single point.

10.2.4 The analyst may include a full 5 point calibration for any of the Arochlors with the initial calibration

10.2.5. The high and low standards for the initial 5 point calibration of 1016 / 1260 define the acceptable quantitation range for the other Arochlors. If any Arochlor is determined above this concentration the extract must be diluted and reanalyzed.

10.2.6. If the analyst knows that a specific Arochlor is of interest for a particular project, that Arochlor may be used for the five point calibration rather than the 1016 / 1260 mix.

10.2.7. The surrogate calibration curve is calculated from the Aroclor 1016/1260 mix. Surrogates in the other calibration standards are used only as retention time markers.

10.2.8. Two options are possible for quantitation of Aroclors. The same quantitation option must be used for standards and samples.

10.2.8.1. Multiple peak option

Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per Aroclor, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

10.2.8.2. Total area option

The total area of the standards and samples may be used for quantitation of multi-component analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multi-component pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

10.3. 12 hour Calibration

The 12 hour calibration verification must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration.

10.3.1. At a minimum, the 12 hour calibration includes analysis of the Arochlor 1260 / 1016 mix.

10.3.2. It is adequate to verify calibration with a mixture of Aroclors 1016 and 1260. If a specific Aroclor is expected, it may be included in the daily calibration check.

10.3.3. The retention time windows for any analytes included in the daily calibration and CCVs are updated.

10.3.4. For this method samples must be bracketed with successful calibration verification runs.

10.4. Calibration verification

The Arochlor 1260/1016 calibration mix is analyzed as the calibration verification standard. This is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. (Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.).

10.4.1. A mid level standard is used for the calibration verification.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001NC.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001NC.

11.4. Suggested gas chromatographic conditions are given in Table C-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table C-5.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Identification of Arochlors

Retention time windows are used for identification of Arochlors, but the "fingerprint" produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

A clearly identifiable Arochlor pattern serves as confirmation of single column GC analysis. Dual column confirmation may be used for specific program requirements or by client request.

12.2. Quantitation of Arochlors

Use 3-10 major peaks or total area for quantitation

If the analyst believes that a combination of Aroclor 1254 and 1260, or a combination of 1242, 1248 and 1232 is present, then only the predominant Arochlor is quantitated and reported, but the suspicion of multiple Aroclors is discussed in the narrative. If well separated Aroclor patterns are present, and then both Aroclors are quantitated and reported

12.3. If there are no interfering peaks within the envelope of the Arochlor, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

12.4. Second column confirmation of Aroclors will only be performed when requested by the client. The appearance of the multiple peaks in the sample usually serves as a confirmation of Aroclor presence.

12.5. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX). Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced under Section 13.1 of the main body of this SOP

13 2 Method detection limits (MDL) are determined for all Arochlors.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Update III, December 1996, Method 8082

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Method 8082 includes limited direction for congener specific quantitation. This is outside the scope of this SOP.

17.2. Modifications from Previous Revisions

No changes were made to this Appendix

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17.3. Tables

Table C-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aroclor-1016	1.0	33	1000
Aroclor-1221	1 0	33	1000
Aroclor-1232	1.0	33	1000
Aroclor 1242	1.0	33	1000
Aroclor-1248	1.0	33	1000
Aroclor-1254	1.0	33	1000
Aroclor-1260	1.0	33	1000

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	10 mL
Low-level Soil	30 g	10 mL
High-level soil / waste	1 g	10 mL

Table C-2

Parameter	Recommended Conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold
Column 1	DB-5 or Rtx-5 30m x 0 32mm id, 0 5µm
Column 2	DB-1701 or Rtx 1701 30m x 0.32 mm id, 0 25µm
Column 3	DB-608, 30m X 0 32 mm, 0.25µm
Injection	1-2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table C-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[1]
Aroclor 1016/1260	100	200	500	1000	2000	4000
Aroclor 1242[2]			500			
Aroclor 1221 +1254[2]			500			
Aroclor 1232[2]			500			
Aroclor 1248[2]			500			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.
[2] Aroclors may be quantitated within the range 100 to 2000 ng/mL (4000ng/mL if the level 6 1016/1260 standard is included) If the Aroclor is more concentrated, it must be reanalyzed at a dilution.

Table C-4			
LCS/Matrix Spike and Surrogate Spike levels for Aroclor analysis with Acid Cleanup µg/L or µg/kg			
	Aqueous	Soil	Waste
Aroclor 1016/1260	10	333	10,000
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6 67	200

Table C-5 Michigan Analyte List and Reporting Limits[1]		
	Reporting Limit	
Compound	water (µg/L)	soil (µg/Kg)
Aroclor-1016	0.2	330
Aroclor-1221	0.2	330
Aroclor-1232	0 4	330
Aroclor 1242	0.2	330
Aroclor-1248	0.2	330
Aroclor-1254	0.2	330
Aroclor-1260	0.2	330

[1] Reporting Limits are only for samples performed under the Michigan program

Table C-5
Suggested Analytical Sequence

Initial Calibration

Injection #		
1	Solvent blank (optional)	
2	Aroclor 1016/1260	Level 1
3	Aroclor 1016/1260	Level 2
4	Aroclor 1016/1260	Level 3
5	Aroclor 1016/1260	Level 4
6	Aroclor 1016/1260	Level 5
7	Aroclor 1232	Level 3
8	Aroclor 1242	Level 3
9	Aroclor 1248	Level 3
10	Aroclor 1221/1254	Level 3
11-30	Sample 1-20 (or as many samples as can be analyzed in 12 hours Solvent blank (optional)	
32	Aroclor 1016/1260	Level 3

etc

Note: A solvent blank or primer may be analyzed at any time during the sequence when highly contaminated samples are expected. A solvent blank or primer may not be analyzed as routine immediately prior to standards.

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Aroclor 1260 / 1016 mix. Mid level standards of any other Aroclors expected to be present in the samples are also injected.

ANALYSIS OF PHENOXY ACID HEBICIDES BASED ON SW-846 METHOD 8151A and 615

1. SCOPE AND APPLICATION

This method is applicable to the gas chromatographic determination of Chlorinated phenoxy acid herbicides in extracts prepared by SOP CORP-OP-0001NC. The herbicides listed in Table D1 are routinely analyzed. Other chlorinated acids may be analyzed by this method if the quality control criteria in Section 9 and the initial demonstration of method performance in Section 13 are met.

1.1. The associated LIMS method code is QS.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of phenoxy acid herbicides by gas chromatography. The herbicides, as their methyl esters, are injected onto the column, separated, and detected by electron capture detectors. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences.

4.2. Chlorinated acids and phenols cause the most direct interference with this method.

4.3. Sulfur may interfere and may be removed by the procedure described in SOP#CORP-OP-0001NC

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A Ni_{63} electron capture detector is required.

6.2. Refer to Table D2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to section 7 of the 8000B section of this SOP for general information on reagents and standards.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table D-3 for the components and levels of the LCS and MS mixes.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements

10.2. Calibration standards are prepared from purchased standards in the methyl ester form.

10.3. The low level standard must be at or below the laboratory reporting limit. Other standards are chosen to bracket the expected range of concentrations found in samples, without saturating the detector or leading to excessive carryover.

10.4. Refer to Table D-2, for details of GC operating conditions.

11. PROCEDURE

11 1 Refer to the method 8000B section of this SOP for procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP #CORP-OP-0001NC.

11.3. Cleanup

The alkaline hydrolysis and subsequent extraction of the basic solution described in the extraction procedure provides an effective cleanup.

11.4 Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

11.4.1 The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

11.4.2. The daily calibration consists of mid level standards of all analytes of interest. Retention time windows must be updated with the daily calibration.

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

11.5. Gas Chromatography

Chromatographic conditions are listed in Table D-2.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes

12 2. The herbicides are analyzed as their methyl esters, but reported as the free acid. For this reason it is necessary to correct the results for the molecular weight of the ester versus the free acid. This is achieved through the concentrations of the calibration standards. For example the 20µg/L calibration standard for 2,4-D contains 21.3 µg/L of the methyl ester. No further correction is necessary

12.3. A routine 10X dilution occurs on final extracts for all samples. Due to a QuantIMS limitation, the dilution factor field in QuantIMS cannot be used when a dilution is routine, because the dilution factor is automatically applied to all reference values creating reporting problems. For the herbicide analysis, the extract volume will be 10mL and an aliquot at 10X dilution will be analyzed. The final extract volume recorded on the laboratory bench sheet will be recorded as 100mL to avoid using the dilution factor field in QuantIMS.

13. METHOD PERFORMANCE

13.1. The EPA for this method has not published multiple laboratory performance data Performance limits for the four replicate initial demonstration of capability are required as referenced under Section 13.1 of the main body of this SOP.

14. POLLUTION PREVENTION

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

Method 8151A, SW-846, Update III, December 1996

17. MISCELLANEOUS

17.1. Modifications from Reference Method

Refer to the method 8000B section of this SOP for modifications from the reference method.

17.2. Modifications from Previous Revision

The calibration procedure has been changed to require esterification of the calibration standards

17.3. Tables

Table D-1				
Standard Analyte list				
Compound	CAS Number	Reporting Limit, µg/L or µg/kg		
		Aqueous	Soil	Waste
2,4-D	94-75-7	4	80	4000
2,4-DB	94-82-6	4	80	4000
2,4,5-TP (Silvex)	93-72-1	1	20	1000
2,4,5-T	93-76-5	1	20	1000
Dalapon	75-99-0	2	40	2000
Dicamba	1918-00-9	2	40	2000
Dichloroprop	120-36-5	4	80	4000
Dinoseb	88-85-7	0 6	12	600
MCPA	94-74-6	400	8000	400,000
MCPP	93-65-2	400	8000	400,000

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol	Final Vol	Dilution Factor
Ground water	1000 mL 10 mL	20	
Low-level Soil without GPC	50 g	10 mL	20
High-level soil / waste	1 g	10 mL	20

Specific reporting limits are highly matrix dependent. The reporting limits listed above are provided for guidance only and may not always be achievable For special projects, the extracts may be analyzed without any dilution, resulting in reporting limits 20 times lower than those in Table D-1.

Table D-2	
Instrumental Conditions	
PARAMETER	Recommended conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	80,2/30/170,0/1/180,1
Column 1	DB-5MS or RTX 5 30x0.32, 0.5um
Column 2	DB-1701 or Rtx-1701
Injection	1-2µL
Carrier gas	Helium / Hydrogen
Make up gas	Nitrogen

Recommended conditions should result in resolution of all analytes listed in Table D-1.

The reporting limits listed in Table D-1 will be achieved with these calibration levels and a 20 fold dilution of the sample extract. Lower reporting limits can be achieved with lesser dilutions of the sample extract.

Table D-3			
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg[1]			
	Aqueous	Soil	Waste
2,4-D	16	800	16000
Silvex	4	200	4000
2,4,5-T	4	200	4000
2,4-DB	16	800	16000
Dalapon	8	400	8000
DCAA (surrogate)	16	800	16000

[1] LCS, MS and SS spikes are as the free acid.

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of the concentration of certain Organophosphorus Pesticides in waters, wastewaters, oils, soils, and sludges. It is based on SW846 Method 8141A. Table E1 shows reporting limits for compounds routinely analyzed by this method The compounds include, but are not limited to, those shown in Table E1.

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

1.3. The associated LIMS method code is P2

2. SUMMARY OF METHOD

2.1. An aliquot of prepared sample is injected in a gas chromatograph (GC) and compounds in the effluent are detected by a flame photometric detector. Appropriate preparation techniques are described in SOP CORP-OP-0001NC. Ultrasonic Extraction (Method 3550) is **NOT** an appropriate sample preparation for Method 8141 and should not be used because of the potential for destruction of target analytes during the ultrasonic extraction process.

3. DEFINITIONS

Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences.

4.2 Analytical difficulties encountered for target analysis include.

4.2.1. The water solubility of Dichlorvos (DDVP) is 10 g/L at 20°C, and recovery is poor from aqueous solution.

4.2.2. Naled is converted to Dichlorvos (DDVP) on column by debromination. This reaction may also occur during sample workup.

4.2.3. Trichlorfon rearranges and is dehydrochlorinated in acidic, neutral, or basic media to form Dichlorvos (DDVP) and hydrochloric acid If this method is to be used for the determination of organophosphates in the presence of Trichlorfon, the analyst should be aware of the possibility of rearrangement to Dichlorvos to prevent misidentification.

4.2.4. Merphos is a single component pesticide that is readily oxidized to Merphos oxone. Chromatographic analysis of Merphos almost always results in two peaks.

5. SAFETY

5.1. Refer to Section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP.

6.2. Refer to Table E2 for Instrument settings.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to Section 7 of the 8000B section of this SOP for general information on reagents and standards.

7.2. Refer to Table E-3 for details of calibration and other standards.

7.3. Surrogate Standards

Triphenyl phosphate is the surrogate standard. Refer to Table E-4 for details of the surrogate standard

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

Refer to section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table E-4 for the components and levels of the LCS and MS mixes.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Calibration standards are made up from purchased solutions. Table E-3 lists the calibration levels.

10.3. The low level standard must be at or below the laboratory reporting limit Other standards are chosen to bracket the expected range of concentrations found in samples, without saturating the detector or leading to excessive carryover

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP #CORP-OP-0001NC.

11.3. Cleanup

11.4. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration

11.4 1 The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

11.4.2. The daily calibration consists of mid level standards of all analytes of interest. Retention time windows must be updated with the daily calibration.

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. Surrogate recovery results are calculated and reported for Triphenylphosphate unless it is determined that sample interference has adversely affected the quantitation of one of the surrogates The surrogate must be within QC criteria. Corrective action is only necessary if Triphenylphosphate is outside of acceptance limits.

13. METHOD PERFORMANCE

13 1 Performance limits for the four replicate initial demonstration of capability are required as referenced under Section 13.1 of the main body of this SOP.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15 1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required

16. REFERENCES

SW846, Update III, December 1996, Method 8141A.

17. MISCELLANEOUS

17.1. Reporting limits

17.1.1. The lower standard reporting limits are listed in Table E-1

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17 1 2 1 The nature of the FPD detector contributes to high dilutions for Method 8141A. There is a phenomenon known as quenching that occurs. This happens when light absorption occurs in the flame of the FPD due to hydrocarbons, sulfur, and certain light absorbing compounds. When this happens the analytes of interest do not reach the photomultiplier tube and are not detected even though they may be present

17.2. Elution time

17.2.1. For any positive detection in a sample, the chromatogram is overlaid on screen with the nearest standard for elution time matching and pattern recognition using the Target system.

17.3. Troubleshooting guide

17.3.1. Consult the instrument manufacturer's operating manual for guidance.

Table E1: Organophosphorus Pesticides Routinely Analyzed and Reporting Limits

Compound	CAS Number	Reporting Limits	
		Water, µg/L	Solid, µg/kg
Azinphos methyl	86-50-0	1.0	33
Bolstar (Suprofos)	35400-43-2	1.0	33
Chlorpyrifos	2921-88-2	1.0	33
Coumaphos	56-72-4	1..0	33
Demeton, O and S	8065-48-3	1.0	33
Diazinon	333-41-5	1.0	33
Dichlorvos	62-73-7	1.0	33
Disulfoton	298-04-4	1.0	33
Ethoprop	13194-48-4	1.0	33
Fensulfothion	115-90-2	1.0	33
Fenthion	55-38-9	1.0	33
Malathion	121-75-5	1.0	33
Merphos	150-50-5	1.0	33
Methyl Parathion	298-00-0	1.0	33
Mevinphos	7786-34-7	1.0	33
Naled	300-76-5	1.0	33
Phorate	298-02-2	1.0	33
Ronnel	299-84-3	1.0	33
Stirophos	22248-79-9	1.0	33
Tokuthion	34643-46-4	1.0	33
Trichloronate	327-98-0	1.0	33
O,O,O-Trientyl phosphorothioate	126-68-1	1.0	33
Thionazin	297-97-2	1.0	33
Sulfotepp	3689-24-5	1.0	33
Dimethoate	60-51-5	1.0	33
Parathion	56-38-2	1.0	33
Famphur	52-85-7	1.0	33

Table E2: Instrumental Conditions	
PARAMETER	Recommended conditions
Injection port temp	175°C
Detector temp	230°C
Initial temp	135°C
Temperature program	(A) 5°C/minute (B) 20°C/minute
Final Temp	(A) 245°C (B) 295°C
Final Hold Time	(A) 0 minutes (B) 7 minutes
Column 1	RTX-OPP, 30 meter, 0.32 mm, 0 5 µm film
Column 2	RTX-1, 30 meter, 0 32 mm, 0 5 µm film
Injection	1-2µL
Carrier gas	Helium / Hydrogen
Make up gas	Nitrogen

Table E3 Initial Calibration Concentrations (ng/uL)

COMPOUND	LEVEL1	LEVEL2	LEVEL3	LEVEL4	LEVEL5	LEVEL6	LEVEL7
o,o,o-Triethylp-hosphate	0.2	0.5	1	2	5	10	20
Dichlorvos	0.2	0.5	1	2	5	10	20
Mevinphos	0.2	0.5	1	2	5	10	20
Thionazin	0.2	0.5	1	2	5	10	20
Ethoprop	0.2	0.5	1	2	5	10	20
Naled	0.2	0.5	1	2	5	10	20
Sulfotepp	0.2	0.5	1	2	5	10	20
Phorate	0.2	0.5	1	2	5	10	20
Demeton	0.2	0.5	1	2	5	10	20
Dimethoate	0.2	0.5	1	2	5	10	20
Diazinon	0.2	0.5	1	2	5	10	20
Disulfoton	0.2	0.5	1	2	5	10	20
Methyl Parathion	0.2	0.5	1	2	5	10	20
Ronnel	0.2	0.5	1	2	5	10	20
Fenthion	0.2	0.5	1	2	5	10	20
Chlorpyrofos	0.2	0.5	1	2	5	10	20
Parathion	0.2	0.5	1	2	5	10	20
Malathion	0.2	0.5	1	2	5	10	20
Trichloronate	0.2	0.5	1	2	5	10	20
Merphos	0.2	0.5	1	2	5	10	20
Stirophos	0.2	0.5	1	2	5	10	20
Tokuthion	0.2	0.5	1	2	5	10	20
Fensulfothion	0.2	0.5	1	2	5	10	20
Bolstar	0.2	0.5	1	2	5	10	20
Famphur	0.2	0.5	1	2	5	10	20
Azinphos methyl	0.2	0.5	1	2	5	10	20
Coumaphos	0.2	0.5	1	2	5	10	20

Table E4: LCS/Matrix Spike and Surrogate Spike Compounds – 20 ug/mL	
Compound	**Compound**
Thinazin	Sulfotepp
Phorate	Disulfoton
Methyl Parathion	Parathion
Famphur	O,O,O-Triethylphosphate
Dimethoate	Triphenyl Phosphate - Surrogate

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1. Scope and Application

1.1. This method is applicable to the determination of the concentration and **tentative** identification of petroleum hydrocarbon mixes in waters, wastewaters, soils, and sludges.

1.2. This SOP is based on SW-846 Method 8015B, Modified, Revision 3, December 1996.

1.3. The associated LIMS method codes are HS (8015 MOD) and KI (8015B).

2. Summary of Method

2.1. This method provides gas chromatographic conditions for detection and identification of total petroleum hydrocarbons. Prior to the use of this method, appropriate sample preparation techniques are used

2.2. An aliquot of the prepared sample is injected into a gas chromatograph (GC) and compounds in the effluent are detected by a flame ionization detector (FID).

2.3. The carbon range for Ohio VAP and BUSTR projects is C10-C20 and C20-C34.

3. Definitions

3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM), current version.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences.

5. SAFETY

5.1 Refer to Section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1 Refer to Section 6 of the 8000B section of this SOP.

6.2 Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to Section 7 of the 8000B section of this SOP.

7.2. The petroleum hydrocarbons are purchased from a chemical supplier when available. When no chemical supplier is available, the fuels are purchased from public sources.

7.3. The OVAP and BUSTR standard is a commercially prepared standard containing alkanes from C10-C34.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

8.1 Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. MS/MSD recoveries are calculated from a Diesel calibration.

9.3. Surrogates

9.3.1. Because of the nature of the TPH analysis, whereas certain petroleum mixtures can override the C9 surrogate, the C9 surrogate recoveries are advisory. Re-extraction due to surrogate recoveries is determined by analyst judgement.

NOTE: Ohio VAP rules require reanalysis when surrogate recoveries are outside of control limits.

10. CALIBRATION AND STANDARDIZATION

10.1. Recommended Instrument Conditions

10.1.1. Hydrogen carrier gas - flow rate 5 - 6 mL/min

10.1.2. Detector gas mixture - air hydrogen mixture in a 10:1 ratio, air 80 - 120 mL/min, hydrogen 8 -12 mL/min

10.1.3. Temperature Program - refer to Appendix

10.1.4. Injection volume - 1 µL

10.2. Initial Calibration

10.2.1. Analyze a five point Diesel calibration standard referring to the recommended instrument conditions. The calibration concentrations are 100, 200, 500, 1000, and 2000 ng/uL. A 5000ng/uL standard may be analyzed if needed. The retention time window of C10-C32 shall be used for the Diesel calibration.

10.2.2. For Ohio VAP and BUSTR calibrations, analyze a five point calibration for the carbon range C10-C20. The concentrations are 60, 120, 240, 600 and 1200 ug/mL. Analyze a five point of the carbon range C20-C34. The concentration ranges are 80, 160, 320, 800, and 1600 ug/mL.

10.3. Continuing Calibration

10.3.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP #CORP-OP-0001NC.

11.3. Cleanup

11.4. Analytical Sequence – Refer to Section 11 in the 8000B Section of this SOP.

11.5. Petroleum Hydrocarbon Identification and/or Fingerprinting

11.5 1. To identify the type of petroleum hydrocarbon, compare the chromatographic peak pattern to the patterns of known petroleum hydrocarbons analyzed under identical chromatographic conditions. Samples are quantified against diesel, but fingerprinting may be done when client requested.

11.5 2. Positive matching may not be possible, even using site-specific hydrocarbons. Degradation of the pattern can occur during environmental exposure of the fuel. See Table 2 for possible fingerprints.

11.6. Sample Quantification

11.6.1. Samples are quantified against the initial calibration of diesel or DRO on a single column.

11.6.2. The total height or area of the hydrocarbon is determined in the same manner used for the hydrocarbon standard.

11.6.3. If the amount of sample injected into the GC exceeds the working range of the calibration curve, an appropriate dilution is performed before reanalysis

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes

12.2. Surrogate recovery results are calculated and reported for Nonane (C-9) unless it is determined that sample interference has adversely affected the quantitation of one of the surrogates The surrogate must be within QC criteria. Corrective action is only necessary if Nonane (C-9) is outside of acceptance limits.

13. METHOD PERFORMANCE

13 1. Performance limits for the four replicate initial demonstration of capability are required as referenced under Section 13.1 of the main body of this SOP.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Method 8015B, Nonhalogenated Organics Using GC/FID, Test Methods for Evaluating Solid Waste, Third Edition, USEPA

16.2. Related SOP

16.2.1. CORP-OP-0001NC, Extraction and Cleanup of Organic Compounds from Waters and Soils, Based on SW846 3500 Series, 3600 Series, 8150, 8151, and 600 Series Methods

Table F1: Suggested GC Temperature Program for TPH analysis

Initial Temperature	40°C
Initial Hold Time	4 minutes
Temperature Program	10°C/minute
Final Temperature	280°C
Final Hold Time	10 minutes

Table F2: Reporting Limits for TPH Analysis

Analyte	Reporting Limits		
	Water (µg/L)	Solids (mg/kg)	Waste Dilution (mg/kg)
TPH (as Diesel) or DRO	100	3.3	200
C10-C20 (OVAP & BUSTR)	60	2.0	
C20-C34 (OVAP & BUSTR)	80	2.3	
Fingerprint Compounds[1]			
Mineral Spirits	Kerosene	Motor Oil	
Hydraulic Oil	Jet Fuel	Stoddard Solvent	
DRO Spiking Solution			
Decane	Dodecane	Tetradecane	
Hexadecane	Octobecane	Eicosane	
Docosane	Tetracosane	Hexacosane	
Octacosane			

[1] This list represents most of the common petroleum hydrocarbons. The list may be expanded to include other petroleum hydrocarbons.

8771440

1. Scope and Application

1.1. This method is applicable to the determination of the concentration of various Non-halogenated Organic Compounds in waters, wastes, sludges, and solids. It is based on SW-846 Method 8015B.

1.2. The applicable LIMs method codes are J7 (GC/FID 8015) and QU (Semivolatile Organics, 8015B). The preparation code is 88.

2. Summary of Method

2.1. This method provides gas chromatographic conditions for the detection of various nonhalogenated organic compounds. Samples are introduced to the GC by direct injection. Detection is achieved by a flame ionization detector (FID).

3. Definitions

3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM).

4. INTERFERENCES

4.1 Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP.

6.2. Recommended Columns:

6.2.1. RTX Stabilwax, fused silica, 60 m x 0.53, 0.5 µm film thickness, or equivalent column.

6.2.2. Stabilwax-DA, fused silica, 60 m x 0.32, 0.5 µm film thickness, or equivalent column.

6.3. Detectors: Flame ionization (FID)

6.4. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to Section 7 of the 8000B section of this SOP

7.1.1 Reagent water

7.2. Standards

7.2.1. Refer to Table G2.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

8.1. Refer to section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

10. CALIBRATION AND STANDARDIZATION

10.1. Recommended Instrument Conditions

10.1.1. The following conditions are recommended. The following table lists specific information for various compounds.

10.1.2. RTX- Stabilwax and Stabilwax-DA Columns:

Carrier Gas:	Hydrogen
Initial Temp:	45 °C
Initial Hold:	3 mins
Ramp Rate A:	5 °C/min
Ramp Rate B:	30 °C/min
Final Hold A:	0 min
Final Hold B:	3 mins
Analysis Time:	17.83 mins
Injector Temp:	275 °C
FID Temp:	300 °C
Injection Vol:	1 µL

10.2. Initial Calibration

10.2.1. For each non-halogenated organic compound and surrogate standard, analyze five or more calibration standards referring to the recommended GC conditions in Section 10.1. One of the standards analyzed should be at or near the concentration which corresponds to the calibration range.

10.2.2. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for procedural requirements.

11.2. Sample Preparation Summary

11.2.1. Samples received fall into three general categories: waters, soils, or wastes.

11.3. Sample Preparation Procedure

11.3.1. Waters

11.3.1.1. Add surrogate solution to the sample to achieve a concentration of 100 mg/L.

11.3.2. Sediments/soils and waste

11.3.2.1. Mix the contents of the sample container with a narrow metal or wood spatula. Weigh 5 g (wet weight) into a tarred culture tube. Use a top-loading balance. Record the weight to 0.01 gram.

11.3.2.2. Quickly add 5 mL of reagent water Add surrogate standard. Cap the vial and vortex to mix for two minutes.

11.3.2.3. If extract is cloudy or has suspended sediment particles, refrigerate and allow sample to sit for a maximum of 24 hours. Filter sample if necessary.

11.4. Sample Analysis

11.4.1 Preliminary Evaluation

11.4.1.1. The sample or sample extract is introduced to the GC column by direct inject techniques The concentration of the sample components is then calculated from the resulting chromatograms.

11.4.2 Analytical Sequence – Refer to Section 11 in the 8000B Section of this SOP.

11.4.3. Inject 1 µL of the sample extract or diluted sample into the GC using the same operating conditions and techniques as those used in the calibration of the instrument.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method

11.5.2. All standards are logged into a department standard logbook. All standards are assigned a unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Refer to the 8000B section of this SOP for identification and quantitation of single component analytes

12.2. Surrogate recovery results are calculated and reported unless it is determined that sample interference has adversely affected the quantitation of the surrogate. The surrogate must be within QC criteria Corrective action is only necessary if the surrogate is outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced under Section 13.1 of the main body of this SOP.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Method 8015B, Nonhalogenated Organics Using GC/FID, Test Methods for Evaluating Solid Waste, Third Edition, USEPA

17. Miscellaneous (Tables, Appendices, Etc...)

Table G1 Non-halogenated Organic Compounds, Reporting Limits[1]

Compound	CAS Number	Reporting Limits	
		Water, mg/L	Solid, mg/kg
2-Methoxyethanol	109-86-4	1.0	1.0
Methanol	67-56-1	1.0	0.5
Isopropyl alcohol	67-63-0	1.0	0.5
n-Propyl alcohol	71-23-8	1.0	0.5
Ethanol	64-17-5	1.0	0.5
n-Butanol	71-36-3	1.0	0.5
1,4-Dioxane	123-91-1	1.0	0.5
Ethylene oxide	75-21-8	1.0	0.5
iso-Butanol	78-83-1	1.0	0.5

[1] If samples require dilution or smaller volumes than specified in this method, the RL will be elevated

Table G2 Non-halogenated Organic Compounds Working Standards

COMPOUND	LEVEL1	LEVEL2	LEVEL3	LEVEL4	LEVEL5	LEVEL 6
2-Methoxyethanol	1.0	2.0	5.0	10.0	20.0	50.0
Methanol	1.0	2.0	5.0	10.0	20.0	50.0
Isopropyl alcohol	1.0	2.0	5.0	10.0	20.0	50.0
n-Propyl alcohol	1.0	2.0	5.0	10.0	20.0	50.0
Ethanol	1.0	2.0	5.0	10.0	20.0	50.0
n-Butanol	1.0	2.0	5.0	10.0	20.0	50.0
1,4-Dioxane	1.0	2.0	5.0	10.0	20.0	50.0
Ethylene oxide	1.0	2.0	5.0	10.0	20.0	50.0
iso-Butanol	1.0	2.0	5.0	10.0	20.0	50.0

1. Scope and Application

1.1. This method is applicable to the determination of the concentration of Sulfolane and N-Methyl-2-pyrrolidone in water and solid samples. It is based on SW846 Method 8015B. The working linear range is 50 to 1000 µg/L. Table H1 lists the reporting limits associated with this method.

1.2. The applicable LIMS method code is KU.

2. Summary of Method

2.1. This method provides gas chromatographic conditions for the detection of mg/L levels of Phillips 66 compounds in water. Prior to use of this method, appropriate sample extraction techniques must be used.

3. Definitions

3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM), current version.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.2.1. Chemicals that have been classified as **carcinogens,** or **potential carcinogens,** under OSHA include: **Methylene Chloride.**

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP.

6.2. Gas Chromatograph

6.2.1. Gas Chromatograph: Modified to accept capillary columns

6.2.2. Data System: Capable of peak integration

6.2.3. Gas Chromatographic Column: 30 m x 0.32 mm ID RTX-5 fused silica capillary column

6.2.4. Autosampler: Capable of reproducible injections

6.2.5. Carrier Gas: Hydrogen

6.2.6. Detector: Flame ionization (FID)

6.3. Volumetric Flasks: 10, 50, and 100 mL

6.4. Microsyringe: 10 µL

6.5. Pipettes: Disposable µL, Pasteur

6.6. Autosampler Vials: 1 mL with 11 mm crimp cap, Teflon®/silicone septum liner

7. REAGENTS AND STANDARDS

7.1. Refer to Section 7 of the 8000B section of this SOP.

7.2. Reagents

7.2.1. Methylene Chloride: Pesticide grade or equivalent

7.3 Standards

7.3.1. Refer to Section 7 of the 8000B section of this SOP.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

8.1 Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Surrogates are not used for this analysis.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1 Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

11. PROCEDURE

11.1 Refer to the method 8000B section of this SOP for procedural requirements.

11.2. Sample Analysis

11.2.1 Summary

11.2.1.1. The sample extract is injected onto the GC column The compounds are then identified and quantitated

11.2.2. Recommended Instrument Conditions

11.2.2.1. GC Conditions

Initial Temperature:	45°C
Initial Hold Time:	4 minutes
Temperature Program:	15°C/minute
Final Temperature:	300°C, hold 2 minutes
Final Time:	23 minutes
Carrier Gas:	Hydrogen
Injection Volume:	1 µL

11.2.3. Sample Analysis Procedure

11.2.3.1. Preliminary Evaluation

The sample extracts may be screened to determine the level of analyte present. If the level of analyte exceeds the working range of the calibration curve, an appropriate dilution is performed to bring the level within the calibration range.

11.2.4. Inject 1 µL of the sample extract or diluted sample into the GC using the same conditions as those used in calibration.

11.2.5. Identification

11.2.5.1. Analytes of interest are identified by comparing retention times with known standards

11.2.5.2. A single column is used for identification.

11.2.6. Sample Quantification

11.2.6.1. Refer to Section 11 in the 8000B Section of this SOP

11.3. Analytical Documentation

11.3.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.3.2. All standards are logged into a department standard logbook All standards are assigned a unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.3.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced under Section 13.1 of the main body of this SOP.

14. POLLUTION PREVENTION

14.1. Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Method 8015B, Nonhalogenated Organics Using GC/FID, Test Methods for Evaluating Solid Waste, Third Edition, USEPA

17. Miscellaneous (Tables, Appendices, Etc...)

17.1. Reporting limits

17.1.1. The lower reporting limits are shown in Table H1

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

TABLE H1
PHILLIPS 66 REPORTING LIMITS

Compound	Reporting Limits, µg/L
Tetramethylene sulfone (Sulfolane)	50
N-Methyl-2-pyrrolidone	50

Controlled Copy No._____

Implementation Date: 10/13/03

SOP No: CORP-0P-0001NC
Revision No: 4.1
Revision Date: 10/07/03
Page 1 of 82

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: **EXTRACTION AND CLEANUP OF ORGANIC COMPOUNDS FROM WATERS AND SOILS, BASED ON SW-846 3500 SERIES, 3600 SERIES, 8151A AND 600 SERIES METHODS.**

(SUPERSEDES: Revision 4.0 (Dated 02/04/03)

Prepared by:	Thomas R. Fairing Jr	10/9/03 Date
Reviewed by:	Technology Specialist	10/8/03 Date
Approved by:	Quality Assurance Manager	10/8/03 Date
Approved by:	Environmental Health and Safety Coordinator	10/8/03 Date
Approved by:	Laboratory Director	10/9/03 Date
Approved by:	Technical Director	10/9/03 Date

8771450

TABLE OF CONTENTS

List of Appendices:

List of Tables

1. SCOPE AND APPLICATION

This SOP describes procedures for preparation (extraction and cleanup) of semivolatile organic analytes in aqueous, TCLP leachate, and soil matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS). The procedures are based on SW-846 and 600 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1. Extraction procedures for the following determinative methods are covered: 8081A, 8082, 8141A, 8151B, 8270C, 8310, 8015B, 8100, 608, 610, and 625

1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

1.3. Other extraction procedures (PFE, SPE, accelerated Soxhlet, etc.) may be used but are not currently covered in this SOP.

1.4. The applicable LIMS method codes are: P2 (8141A), QJ (8081A), QS (8151A), QL (8270C), SG (8310), DM (608), VT (610), DP (625), A1 (8100), HS (8015B)

2. SUMMARY OF METHOD

2.1. Separatory Funnel Extraction

A measured volume of sample, typically 1 liter, is adjusted, if necessary, to a specified pH and serially extracted with methylene chloride using a separatory funnel.

2.2. Continuous Liquid/Liquid Extraction

A measured volume of sample, typically 1 liter, is placed into a continuous liquid/liquid extractor, adjusted, if necessary, to a specific pH and extracted with methylene chloride for 18-24 hours.

2.3. Sonication Extraction

A measured weight of sample, typically 30 g, is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using an ultrasonic horn.

2.4. Soxhlet Extraction (Accelerated and Traditional)

A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This is extracted with refluxing solvent.

2.5. Cleanup and Concentration

Procedures are presented for removing interferents from sample extracts, and for drying and concentration of the extract to final volume for analysis.

2.6. Phenoxy acid herbicide extractions

Procedures for the extraction and cleanup of phenoxy acid herbicides are presented in Appendix A.

3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the STL North Canton Laboratory Quality Manual (LQM), current version .

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document.

5.2. Eye protection that protects against splash, laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately. Viton gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone]. When good manual dexterity is needed, for example, when handling small quantities/containers, disposable gloves (such as latex or N-DEX®) shall be used. While these gloves protect against splashes, they give little or no protection against contact with large quantities of solvent, and no protection against spills or immersion.

5.3. The following analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'dichlorobenzindine, benzo(a)pyrene, alpha-BHC, beta-BHC, gamma-BHC,

delta-BHC, dibenz(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyl compounds. Primary standards of these toxic compounds should be prepared in hood.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3 2 Mg/M3-Ceiling	This material will cause burns if comes into contact with the skin or eyes. Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid (1)	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain, and severe tissue burns. Can cause blindness.

Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Acetonitrile	Flammable Poison	40 ppm-TWA	Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit. Use of methylene chloride for glassware cleaning should be avoided as far as possible. If more than 500 mL of Methylene chloride is spilled, evacuate the area until the area has been cleaned by EH&S.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints which can become stuck. Technicians must use Kevlar or other cut/puncture resistant gloves when separating stuck joints.

5.9. 3510 Separatory Funnel

5.9.1. The use of separatory funnels to extract aqueous samples with Methylene Chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted, periodic venting may be necessary during the extraction. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, the use of a face shield over safety glasses or goggles is recommended. Keep the sash on the fume hood as low as reasonably possible.

5.10. 3520 Extraction Cont Liq/Liq

5.10.1. All personnel are to ensure liquid-liquid area is clear of unnecessary items. Heating mantles used with liquid- liquid extractions generate temperatures that could ignite some materials that come in contact with the heating mantles.

5.10.2. Ensure all solvents are away from liquid-liquid extractor. Increased temperatures near solvents can cause the pressure in the containers to increase.

5.10.3. Ensure all boiling flasks have cooled to room temperature before disconnecting liquid-liquid bodies from boiling flasks to prevent any burns.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware should be cleaned with soap and water, rinsed with water and dried in an oven at 400°C for at least 2 hours. Alternatively the glassware can be solvent rinsed with acetone or methanol followed by methylene chloride after the water rinse.

6.2. Equipment and supplies for extraction procedures

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
Separatory Funnel: 2 L	√				
Separatory Funnel Rack	√				
Balance: >1400 g capacity, accurate ±1 g	√	√			
pH indicator paper, wide-range: covers extraction pH	√	√			
Graduated cylinder: 1 liter. (other sizes may be used)	√	√			
Erlenmeyer Flask or Fleaker: 125 & 300 mL (other sizes optional)	√		√		
Centrifuge	√				
Auto-Shaker	√				

EQUIPMENT AND SUPPLIES	Sep fun	CLLE	Soni	Sox	Conc
Methylene Chloride Collection Tank	√	√			
Solvent Dispenser Pump or 100 mL Graduated Cylinder	√		√		
Continuous Liquid/Liquid Extractor		√			
Round or flat Bottom: 250, 500 mL or 1 L		√			
Boiling Chips: Contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent).		√		√	√
Cooling Condensers		√		√	
Heating Mantle: Rheostat controlled		√		√	
Auto-timer for heating mantle		√		√	
Beakers: 250 & 400 mL, graduated			√		
450mL wide-mouth glass jars			√		
Balance: >100 g capacity, accurate ±0.1 g			√	√	
Soxhlet Extractor				√	
Cellulose and Glass Thimbles				√	
Accelerated Soxhlet Extractor (Soxtherm-trade name)				√	
Sonicator (at least 300 watts)			√		
Sonicator horn, 3/4 inch			√		
Kuderna-Danish (K-D) Apparatus: 500 mL					√
Concentrator Tube: 10 mL, attached to K-D with clips					√
Snyder Column: Three-ball macro					√
Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.					√
Turbo Vap II					√
Turbo Vap Tube: 200mL capacity					√
Vials: Glass, 2 mL, 4 mL, and 10 mL capacity with Teflon®-lined screw-cap					√
Nitrogen Blowdown Apparatus					√
Nitrogen: reagent grade.					√
Culture tubes: 10 mL, 16 mmx100 mm					√
Syringe: 1 mL	√	√	√	√	
Phase Separation Paper	√	√	√	√	
Glass Wool	√	√	√	√	
Glass Funnel: 75 X 75 mm	√	√	√	√	√
Disposable Pipets	√	√	√	√	√
Aluminum foil	√	√	√	√	√
Paper Towels	√	√	√	√	√
Wrist Shaker					

6.3. Equipment and Supplies for Cleanup Procedures

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	A/B	*FC*
Gel permeation chromatography system (J2 Scientific Accuprep System)	√					
Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent).	√					
Chromatographic column: 700 mm x 25 mm ID glass column. Flow is upward	√					
Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep flow-through cell.	√					
Strip chart recorder, recording integrator, or laboratory data system.	√					
Syringe: 10 mL with Luerlok fitting.	√					
Syringe filter assembly, with disposable 5 um filter discs, Millipore No. LSWP 01300 or equivalent.	√					
Chromatographic column: 250 mm long x 10 mm ID, with Pyrex glass wool at the bottom and a Teflon stopcock (for silica gel cleanup).	√					
Vacuum system for eluting multiple cleanup cartridges. Supelco (or equivalent). The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts.		√				
Vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.		√				
Vacuum pressure gauge.		√				
Rack for holding 10 mL volumetric flasks in the manifold.		√				
Mechanical shaker or mixer: Vortex Genie or equivalent.			√	√		
Separatory Funnels with Ground-Glass Stoppers 250 mL					√	
Erlenmeyer Flasks: 125 mL					√	
Disposable Pipets		√	√	√	√	√
Culture tubes: 10 mL, 16 mmx100 mm	√	√	√	√	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents for Extraction Procedures

All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	Sep fun	CLLE	Soni	Sox	Conc
Sodium hydroxide (NaOH), Pellets: Reagent Grade	√	√			
Sodium hydroxide solution, 10 N: Dissolve 40 g of NaOH in reagent water and dilute to 100 mL.	√	√			
Sulfuric acid (H_2SO_4), Concentrated Reagent Grade	√	√			
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.	√	√			

REAGENTS	Sep fun.	CLLE	Soni	Sox	Conc
Hydrochloric Acid (HCl)					
Organic free reagent water.	√	√			
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 400°C a minimum of two hours.	√	√	√	√	√
Extraction/Exchange Solvents: Methylene chloride, hexane, acetonitrile, acetone, pesticide quality or equivalent	√	√	√	√	√
Acetone: Used for cleaning	√	√	√	√	√

7.2. Reagents for Cleanup Procedures

REAGENTS	GPC	Florisil	Sulfur	Acid	A/B	*FC*
Florisil: 500 mg or 1 g cartridges with stainless steel or Teflon frits (calalog 694-313, Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent.)		√				
Mercury: triple distilled			√			
Tetrabutylammonium hydrogen sulfate			√			
Sodium sulfite			√			
Tetrabutylammonium (TBA) sulfite reagent: Prepare reagent by dissolving 3 39 g of Tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. Extract this solution 3 times with 20 mL portions of hexane. Discard the hexane extracts. Add 25 g sodium sulfite to the water solution.			√			
2-Propanol			√			
Nitric acid: 1N			√			
Copper powder: remove oxides (if powder is dark) by treating with 1N nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen			√			
Sulfuric acid, Concentrated				√		
Sodium hydroxide, Pellets					√	
Sodium hydroxide, 10N: Dissolve 40 g of NaOH in 100 mL of reagent water					√	
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade					√	
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.					√	
Fluorocarbon: PF-5080, 3M						√

7.3. Standards

7.3.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from neats. Semivolatile stock standards are stored at ≤ 6°C. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the

time the ampoule is opened if purchased.) Standards must be allowed to come to room temperature before use.

7.3.2. Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.3. Matrix Spiking and Laboratory Control Spiking Standards.

The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 6. Spiking standards are purchased or prepared as dilutions of the stock standards. Spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.4. GPC calibration solution - prepare or purchase a solution in methylene chloride that contains the following analytes in the concentrations listed below:

Analyte	mg/mL
Corn Oil	25.0
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.2
Perylene	0.02
Sulfur	0.08

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds. This standard has a lifetime of 6 months.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1 Extraction is initiated within 7 days of the sampling date for aqueous samples, 14 days for solid and waste samples.

8.3.2 For TCLP leachates, extraction is initiated within seven days from when the TCLP Leach tumbling has been completed, excluding the filtration step. If the filtration step requires extended times, this time counts as part of the seven day holding time.

8.3.3. Analysis of the extracts is completed within forty days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

9.1.1. The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an LCS and a matrix spike / matrix spike duplicate. (In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS / MSD). If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD. See policy QA-003 for further definition of the batch.

9.2. Definition of matrix

9.2.1. The possible matrix types are aqueous, soil, waste and TCLP leachate.

9.3. Insufficient Sample

9.3.1. If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria. Use of a LCS pair in place of a MS/MSD must be documented.

9.4. Sample count

9.4.1. Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count. Field samples are included.

9.5. Method Blank

9.5.1. A method blank consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the method blank at the same level as the samples. The method blank is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

9.5.2. Aqueous Method Blanks use 1000 mL of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.3. Solid method blanks use 30 g of sodium sulfate spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.4. TCLP method blanks use 250 mL of leachate fluid (100 mL for herbicides) spiked with the surrogates. The leachate may optionally be diluted to 1000 mL with reagent water. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.6. Laboratory Control Sample (LCS)

9.6.1. Laboratory Control Samples are well-characterized, laboratory generated samples used to monitor the laboratory's day to day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure, including any cleanup steps.

9.6.2. The LCS is made up in the same way as the method blank (See sections 9.5.1 - 9.5.4) but spiked with the LCS standard and the surrogates.

9.7. Surrogates

9.7.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.7.2. Each applicable sample, blank, LCS and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining

whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.7.1. A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second spiked aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike.

9.8. Initial Demonstration of Capability

9.8.1. The initial demonstration and method detection limit studies described in section 13 must be acceptable before analysis of samples may begin.

9.9. Quality Assurance Summaries

9.9.1. Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

9.10. STL North Canton QC Program

9.10.1. Further details of QC and corrective action guidelines are presented in the STL North Canton QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure 1.0 mL of solvent into an autovial using a gastight syringe that is manufactured to a certified volume delivery tolerance of ±0.01 mL (1mL total volume). The "standard" autovial is sealed and the top and bottom of the meniscus are marked. The autovials containing the sample extracts are then compared against the "standard" vial to ensure that the final volume is consistently 1.0 ± 0.01 mL. If a new box of autovials are used, then the steps are repeated to further ensure that variations due to vial size and shape are minimized. A log is kept of the lot number of the vials and the day the vials were prepared.

10.2. Refer to section 11.15. for calibration of the GPC. Otherwise this section is not applicable.

11. PROCEDURE

Procedures for separatory funnel liquid/liquid extraction (11.2), continuous liquid/liquid extraction (11.4), sonication extraction (11.5), soxhlet extraction (11.6), accelerated soxhlet (11.7), waste dilution (11.8), extract concentration (11.9), and extract cleanup (11.19) are presented in this section.

11.1. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance memo and approved by a supervisor and QA/QC manager. If contractually required, the client will be notified. The Nonconformance memo will be filed in the project file.

Any deviations from this procedure identified after the work has been completed must be documented as a nonconformance, with a cause and corrective action described. A Nonconformance memo shall be used for this documentation.

11.2. Separatory Funnel Liquid/Liquid Extraction of Water Samples.

A flow chart for this procedure is included in Section 17.

11.2.1. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.2.2. The normal sample volume is 1 liter. Other sample volumes may be used to obtain specific reporting limits, and reduced sample volumes, diluted to 1 liter with reagent water, may be used for very dirty samples.

11.2.3. Weigh the sample container on a balance (± 1 g), taring the sample and container. Transfer the sample to the separatory funnel. . Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (see.Table 4) Mix well. Rinse the sample bottle with 60 mL methylene chloride and transfer to the separatory funnel. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.3.1. If the entire sample bottle will not be used, transfer the aliquot to the separatory funnel, then add the spiking solutions to the sample in the separatory funnel.

Note: Alternative methods of measurement of sample volume include a) transferring the sample to a measuring cylinder and b) marking a meniscus on the sample bottle and then measuring the volume of water required to fill the bottle to the meniscus after the sample is transferred. The former method is not recommended because of the risk of cross contamination while the latter is not recommended because of poor accuracy. However, either method may be necessary for specific client programs.

11.2.4. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The LCS is spiked with the surrogate and matrix spike solutions, the method blank only with the surrogates.

11.2.5. Use 250 mL of leachate for TCLP pesticides and TCLP semivolatiles, measured in a graduated cylinder. An alternative method would be to tare 400ml beaker on the balance and then add 250g to the beaker. Assume a density of 1g/mL and record the volume on the benchsheet. The leachate may be made up to 1 L in volume with reagent water.

11.2.6. For a TCLP method blank, LCS and LCS Dup measure 250 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Add 60 mL of methylene chloride to the separatory funnel. The TCLP leachate may be diluted to approximately 1 liter before extraction if desired.

11.2.7. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper by dipping a disposable pipette into the sample and wetting the pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.2.8. Seal and shake or rotate the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure. An autoshaker may be used to shake and rotate the separatory funnel.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.9. Allow the organic layer to separate from the water phase until complete visible separation has been achieved (approximately 10 minutes). If the

emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. If the emulsion cannot be broken (recovery of <80% of the methylene chloride*), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in continuous liquid-liquid extraction (Section 11.4.). If this is done, the sample must be extracted as part of a valid CLLE batch.

*Note: 15 - 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent.

11.2.10. Fill a funnel with 10-20 g of anhydrous sodium sulfate. The funnel can be plugged with glass wool or filter paper may be used to hold the sodium sulfate. Drain the solvent extract from the separatory funnel through the prepared filtration funnel into a clean glass container. The extract may be drained directly into the KD flask. Close the stopcock just before the water level begins draining out of the separatory funnel. If the sodium sulfate becomes saturated with water add more to the funnel or replace the existing sodium sulfate with fresh drying agent.

11.2.11. Repeat the extraction process two more times using fresh 60 mL portions of solvent, combining the three solvent extracts in the collection container.

11.2.12. If extraction at a secondary pH is required, adjust the pH of the sample in the separatory funnel to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. Serially extract with three 60 mL portions of methylene chloride, as outlined in Steps 11.2.7 to 11.2.9. Collect these three extracts in the same container used for the previous fraction.

11.2.13. Rinse the extract residue from the sodium sulfate by pouring 20-30 mL of clean methylene chloride through the funnel and into the collection container.

11.2.14. Dispose of solvent and water remaining in the extractor into the appropriate waste container.

11.2.15. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.9 for concentration and Section 11.12 for cleanup.

11.3. Short-Term Continuous Liquid-Liquid Extraction

11.3.1. Extraction personnel must first determine if one liter of sample exists in the sample bottle.

11.3.2. Mark the meniscus on the side of the sample bottle for later determination of sample volume.

11.3.3. Add 225 mL methylene chloride to the extractor, turn stopcock to the open position. Connect extractor to a 250 ml boiling flask with boiling chips.

11.3.4. Check the pH of the sample and adjust, if necessary, using 1:1 H2SO4 or 10N sodium hydroxide. Quantitatively transfer the sample from the sample bottle to the extractor. *Rinse the sample bottle with 60-ml of methylene chloride. Pour the rinsate from the sample bottle into the continuous extractor.

11.3.5. Adjust the volume of solvent in the boiling flask by adding reagent water to the extractor, if necessary.

11.3.6. Next, fill the sample bottle to the mark with reagent water. Pour the reagent water into a graduated cylinder. Measure the reagent water to ± 10 ml and document this sample volume on the extraction benchsheet.

11.3.7. Add the appropriate volume of surrogate to each sample and spiking solutions to the MS, MSD, LCS, and/or LCSD in the extractor and mix well.

11.3.8. Extract samples for 12 hours. 8270 extractions will still be performed in two pH extraction steps. Each step will run 6 hours, however, where timing is a factor the samples may be left to extract for longer than 12 hours.

11.3.9. Turn stopcocks to the closed position.

11.3.10. Allow the extractors to run another 5 minutes, then turn off the rheostats and mantles.

11.3.11. The samples will macro concentrate in the CLLE. After the flasks have cooled, continue to concentrate the extracts by KD or QES methodology.

11.3.12 This method of extraction **cannot** be used for method 625, 610 or 608.

11.4 Continuous Liquid/Liquid Extraction from Water Samples.

A flow chart for this procedure is included in Section 17.

11.4.1. Assemble the apparatus. Add 250-400mL of methylene chloride to the extractor body. Add 3 to 5 boiling chips to the round-bottom distilling flask.

11.4.2. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.4.3. Weigh the sample container on a balance (± 1 g), taring the sample and container. Transfer the sample to the continuous liquid/liquid extractor . Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (see.Table 4) Mix well. Rinse the sample bottle with 60 mL methylene chloride and transfer to the continuous liquid/liquid extractor. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, during the rinse for 600 series methodology venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.4.3.1. If the entire sample bottle will not be used, transfer the aliquot to the extractor, then add the spiking solutions to the sample in the extractor.

Note: Alternative methods of measurement of sample volume include: a.) transferring the sample to a measuring cylinder and b.) marking a meniscus on the sample bottle and then measuring the volume of water required to fill the bottle to the meniscus after the sample is transferred. The former method is not recommended because of the risk of cross contamination while the latter is not recommended because of poor accuracy. However, either method may be necessary for specific client programs.

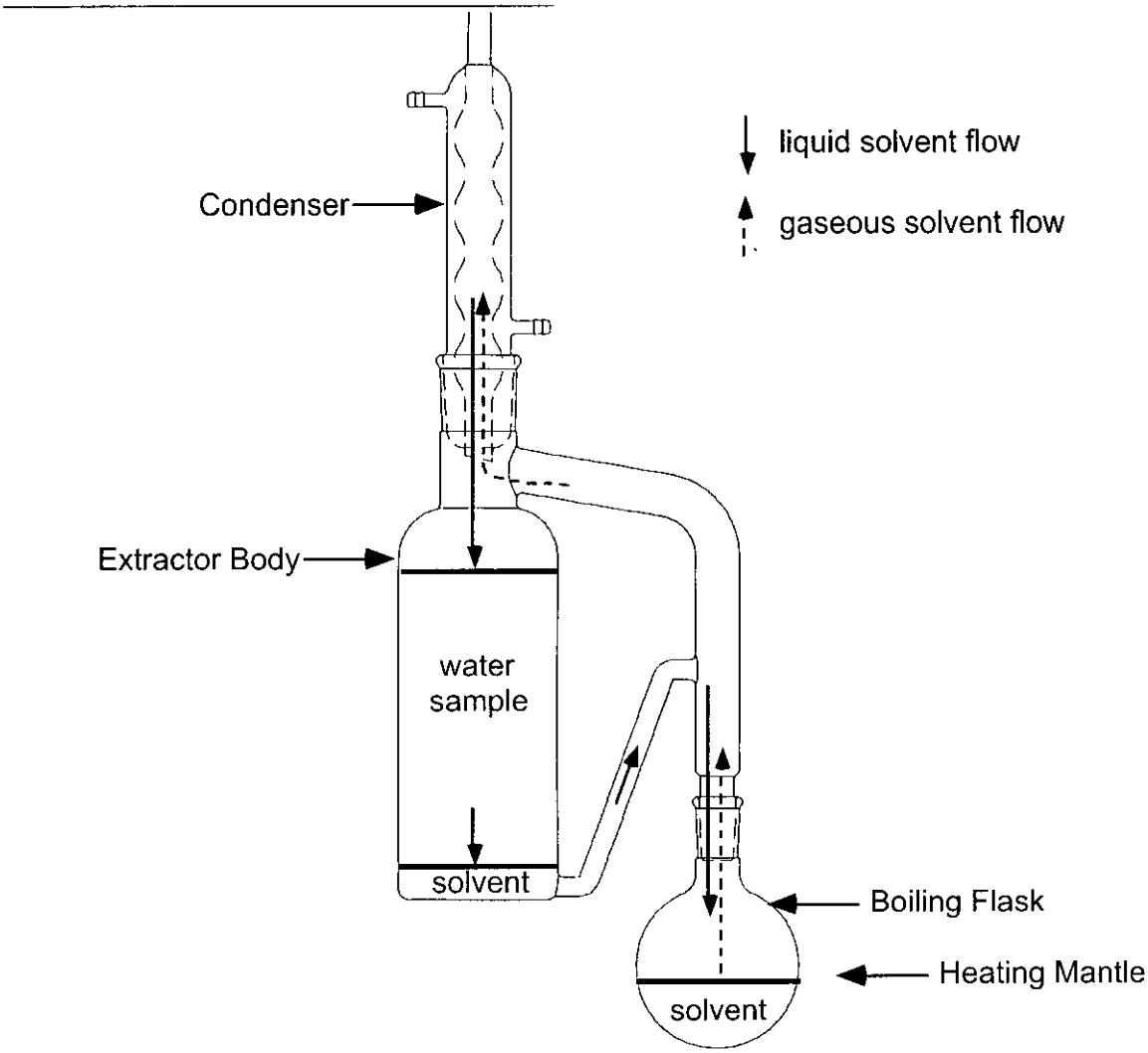
11.4.3.2.Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP. Use 1 L of reagent water for method blanks

and LCS. The method blank is spiked with the surrogates, the LCS and matrix spikes with the surrogates and matrix spiking solutions.

11.4.3.3. Use 250mL of leachate for TCLP for TCLP semivolatiles and TCLP pesticides measured in a graduated cylinder. An alternative method would be to tare 400ml beaker on the balance and then add 250g to the beaker. Assume a density of 1g/mL and record the volume on the benchsheet. Dilute to about 1 liter with reagent water.

11.4.3.4. For a TCLP method blank, LCS and LCS Dup measure 250 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water.

Less than one liter of sample may be used, for highly contaminated samples, or if the reporting limit can be achieved with less than one liter of sample. In this event dilute the sample to about 1 liter with reagent water.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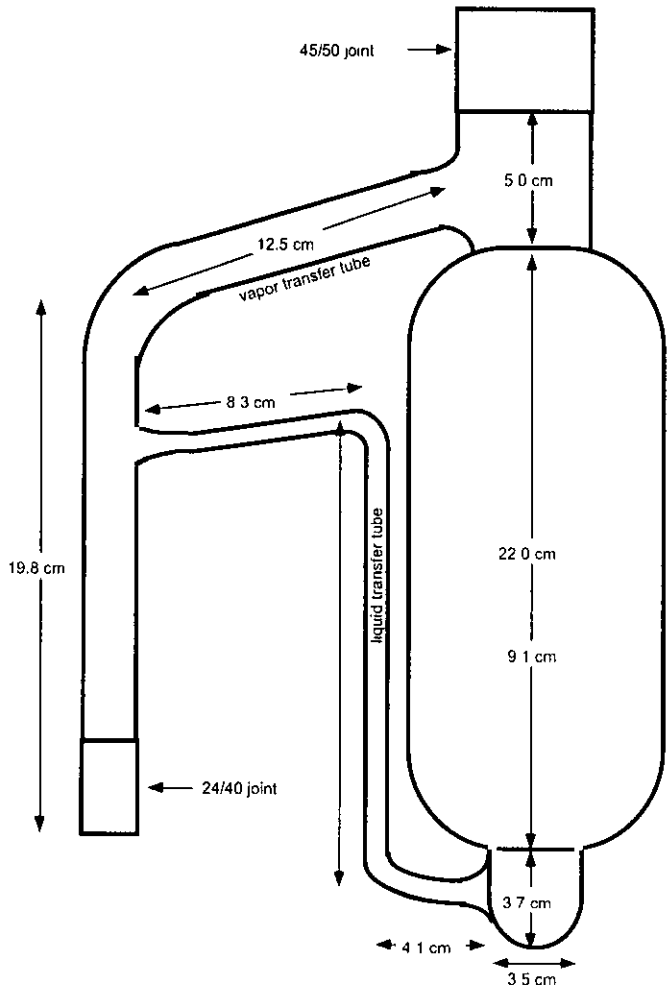
solvent
Boiling Flask
Heating Mantle
solvent



11.4.4. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.4.5. Add reagent water to the extractor body until approximately 250 mL of methylene chloride is pushed over into the round-bottomed flask to ensure proper operation and solvent cycling. Attach cold condenser (about 10°C). Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours. (24 hours required for 600 series)

11.4.6. If extraction at a secondary pH is required, (see Table 1) turn off the heating mantle and allow the extractor to cool. Detach the condenser and adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. Reattach the condenser and turn on heating mantle. Extract for 18-24 hours.

11.4.7. Turn off the heating mantle and allow the extractor to cool.

11.4.8. Place a funnel containing 10-20 g of anhydrous sodium sulfate on the Kuderna-Danish (K-D) apparatus or other glass container. The funnel can be plugged with glass wool enabling it to hold the granular anhydrous sodium sulfate or phase separation filter paper may be used.

11.4.9. Dry the extract in the round bottom flask by filtering it through the sodium sulfate filled funnel. Note that it is not necessary or advisable to attempt to add the solvent remaining in the continuous extractor body to the extract.

11.4.10. Collect the dried extract in a K-D or other glass container. Rinse the funnel with 20-30 mL of methylene chloride to complete the quantitative transfer. Dispose of solvent and water remaining in the extractor in the appropriate waste container.

Note: Some types of CLLE apparatus have built in drying columns. If this type of apparatus is used then a drying step subsequent to the extraction may not be necessary.

11.4.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.9 for concentration and Section 11.12 for cleanup.

11.5. Sonication

A flow chart for this procedure is included in Section 17.

11.5.1. Determination of percent moisture (Optional - if a different group performs this test, refer to the facility SOP.)

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight (at least 12 hours) at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.5.2. Determination of pH (Optional - if a different group performs this test, refer to the facility SOP.)

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for five minutes then let stand for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.5.3. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

11.5.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.5.5. Weigh 30 g of sample ± 0.2g into a 250 or 400 mL beaker. Record the weight to the nearest 0.01 g in the appropriate column on the benchsheet. Use 30 g of sodium sulfate for the method blank and 30 g of sodium sulfate with 30 g of reagent sand for the LCS.

11.5.6. Mix weighed sample with a spatula adding enough anhydrous sodium sulfate (approximately 30 g) to be free flowing. (If the sample is not free flowing extraction efficiency may be reduced)

11.5.7. Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP.

11.5.8. Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (See Table 4) Add 1 mL of the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Refer to Table 6 for details of the surrogate spiking solutions. Add 1 mL of the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS.

Refer to Tables 3 and 5 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

Note: The same volume of surrogate and matrix spiking solution is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

11.5.9. Immediately add a minimum of 100 mL of solvent to the beaker.

Solvents:

Semivolatile GC/MS, TPH, Organochlorine pesticides and PCBs	1:1 Methylene Chloride / Acetone

Note: Steps 11.5.5 - 11.5.9 should be performed rapidly to avoid loss of the more volatile extractables.

11.5.10. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.5.11. Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 6 for the 3/4 inch high gain (Q) horn or 10 for the 3/4 inch standard horn. with mode switch on pulse, and percent-duty cycle knob set at 50%.

Note: Do ***not*** use ***Microtip*** probe.

11.5.12. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.5.13. Place the prepared funnel on a collection apparatus (beaker or K-D Apparatus).

11.5.14. Decant and filter extracts through the prepared funnel into a clean beaker or K-D Apparatus.

11.5.15. Repeat the extraction two more times with additional 100 mL minimum portions of solvent each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone appropriate solvent (Refer to Table in 11.5.9).

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.5.16. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.9 for concentration and Section 11.12 for cleanup.

11.5.17. Sonicator Tuning: Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned at least every time a new horn is installed.

11.6. Soxhlet

11.6.1. Determination of % moisture

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.6.2. Determination of pH

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.6.3. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

11.6.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.6.5. Weigh 30 g of sample ± 0.2g into a beaker, recording the weight to the nearest 0.01 g on the benchsheet.. Use 30 g of sodium sulfate for the method blank and LCS. Add 30 g of anhydrous sodium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet thimble, but do not pack the thimble tightly. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the soxhlet extractor is an acceptable alternative for the thimble.

11.6.6. Add the appropriate amount of surrogate and matrix spiking solution as indicated in Tables 3, 4, 5, and 6.

Sample weights less than 30 g but over 5 g may be used if the appropriate reporting limits can be met.

11.6.7. Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP, using sodium sulfate as the matrix. The weight of sodium sulfate used should be approximately the weight of soil used in each sample.

11.6.8. Place approximately 200mL of solvent into a 250 mL flat bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles per hour. Check the system for leaks at the ground glass joints after it has warmed up.

NOTE: If a reduced quantity of sample is extracted, it is usually necessary to increase the amount of sodium sulfate added or increase the solvent boiling rate to properly set the cycling rate.

Solvents:

Semivolatile GC/MS, OPP, PAH, TPH Organochlorine pesticides and PCBs	1:1 Methylene Chloride / Acetone

11.6.9. Allow the extract to cool after the extraction is complete, then disassemble by gently twisting the soxhlet from the flask. Dry the extract in the flask by filtering it through a sodium sulfate filled funnel.

11.6.10. Collect the dried extract in a K-D or other glass container. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

11.6.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.9 for concentration and Section 11.12 for cleanup.

11.7. Accelerated Soxhlet (Soxtherm Trade Name)

11.7.1. Demonstration of % moisture

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

$$\%Moisture = \frac{\text{(Weight of wet sample – Weight of dry sample)}}{\text{Weight of wet sample}} \times 100$$

11.7.2. Determination of pH
If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for 1 hour. Determine the pH of the sample with a glass electrode and Ph meter.

11.7.3. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible, place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker, return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials, consult with the client (via the Project Manager or Administrator).

11.7.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to return to room temperature.

11.7.5. Weigh 30 g of sample ± 0.2 g into a beaker, recording the weight to the nearest 0.01 g on the benchsheet. Use 30 g of sodium sulfate for the method blank and LCS. Add 30 g of anhydrous sodium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet thimble, but do not pack the thimble tightly. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the thimble is required.

11.7.6. Add the appropriate amount of surrogate and matrix spiking solution as indicated in Tables 3, 4, 5, and 6.

11.7.7. Sample weights less than 30 g, but over 5 g may be used if the appropriate reporting limits can be met.

11.7.8. Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP, using sodium sulfate as the matrix. The weight of sodium sulfate used should be approximately the weight of soil used in each sample.

11.7.9. Place thimble in beaker containing clean boiling chips and add approximately 140 mL of solvent. Place beakers into positions on the accelerated soxhlet unit. Run appropriate program for the extraction solvent. Check the system for leaks at the joints periodically.

Solvents:

Semivolatile MS, PAH, TPH	1:1 Methylene Chloride / Acetone
Semivolatile GC PCB, PEST, OPP	1:1 Hexane/Acetone

11.7.10. Upon completion of the program, remove the beaker from the unit and dispose of the extracted sample. Dry the extract in the flask by filtering it through a sodium sulfate filled funnel.

11.7.11. Collect the dried extract in a K-D, TurboVap tube, or other glass container. Rinse the flask which contained the solvent extract with 10-15 mL of methylene chloride and pour it through the funnel. Rinse the funnel with 10-15 mL of methylene chloride to complete the quantitative transfer.

11.7.12. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.9 for concentration and Section 11.12 for cleanup.

11.8. Waste Dilution

11.8.1. This method is used for materials that are soluble in an organic solvent.

11.8.2. Transfer 10 mL of the solvent to be used for dilution into a Teflon capped vial. Mark the meniscus on the vial, then discard the solvent.

11.8.3. Tare the vial, then transfer approximately 1g of sample to the vial. Record the weight to the nearest 0.01 g.

11.8.4. Add appropriate volume of surrogate and spike solutions (Table 3).

11.8.5. Dilute to 10 mL with the appropriate solvent. (Methylene Chloride for GC/MS- and GCS-TPH. Add 10 mL of appropriate solvent (Hexane) for GCS-pesticide and/or PCB analysis.

11.8.6. Add 2 g + 0.1 g sodium sulfate to the sample. Cap and shake or vortex each extract for 2 minutes.

11.8.7. If H2O is still present, add 4-5 g sodium sulfate to a small pipette funnel. The funnel can be plugged with glass wool or phase separation filter paper may be used to hold the sodium sulfate.

11.8.8. Pour the sample through the funnel, collecting as much as possible in a clean vial. Do NOT rinse the funnel with additional solvent, and do NOT concentrate the sample. The final volume is defined as 10 mL.

11.8.9. Label the sample, which is now ready for cleanup or analysis.

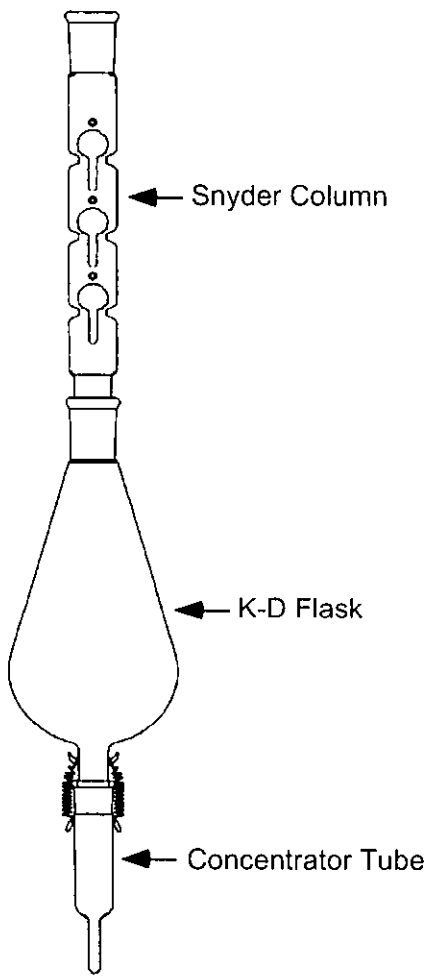
11.9. Concentration

According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

11.9.1. Kuderna-Danish (KD) Method:

11.9.1.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. Transfer the sample to the K-D flask.

11.9.1.2. Add one or two clean boiling chips and the extract to be concentrated to the KD flask and attach a three ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column (this is important to ensure that the balls are not stuck and that the column will work properly).



11.9.1.3. Place the KD apparatus on a water bath (90-98°C) so that the tip of the concentrator tube is submerged. The water level should not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter but the chambers should not flood.

11.9.1.4. Concentrate to 5-15 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent (50 mL hexane, 20 ml hexane/acetone, or 4 mL acetonitrile,4mL toluene (Herbicide TCLP), or 10 mL toluene) to the top of the Snyder Column, and then continue the water bath concentration back down to 1-4 mL. Refer to Table 2 for details of exchange solvents and final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: Add an additional boiling chip with the addition of exchange solvent.

An alternative technique for solvent exchange is to replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to approximately 1 mL, add the appropriate solvent, and concentrate back down to 1 mL. The extract must be cool before the macro Snyder assembly is removed.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.9.1.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.9.1.6. If the final volume is 5 or 10 mL the extract may be made up to volume in the graduated KD tube or transferred to a 12 mL vial previously marked at the appropriate volume level. Document the final volume. Otherwise proceed to Section 11.10

11.10. Nitrogen Evaporation to Final Concentration

11.10.1. Transfer the entire extract to a calibrated evaporation tube. Rinse the concentrator tube with 1-2 mL of the appropriate solvent and transfer the solvent rinsate to the evaporation tube.

11.10.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but should not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C
Toluene	111°C

11.10.3. During the course of the evaporation rinse the sides of the evaporation tube twice with approximately 1 mL of clean solvent. The first rinse should be about half way through he process, with the second rinse when the solvent volume gets close to 1 mL. Concentrate the solvent accurately to the calibrated volume line and transfer the extract to the appropriate storage vial.

Note: It is very important not to concentrate to dryness as analytes will be lost.

An alternative technique is to follow the previous steps concentrating the solvent to slightly below the required final volume and then drawing the extract into a syringe. Rinse the evaporation tube with a small amount of solvent and draw additional solvent into the syringe to make up the accurate final volume.

Note: It is very important not to concentrate to dryness as analytes will be lost.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

Alternative QES Concentration Method:

This concentration method uses a hot water jacketed concentrator tube (CT) instead of the hot water bath and concentrator tube used in Section 11.9.1.1. The construction of the jacketed concentrator tube reduces the tendency of the extract to evaporate to dryness. Thus, low boiling analytes are retained in the extract better with less analyst monitoring of the concentration process.

Assemble the jacketed concentrator tube, KD body and hot water hoses. Add 1mL of exchange solvent (if needed) and one large, clean boiling chip.

***NOTE**: The boiling chips used in the jacketed concentrator tube must be large enough to prevent them falling down into the tip of the CT. If the boiling chip is not in the proper position, the*

extract may superheat and bump vigorously if the extract solvent warms up slowly.

Pour the extract to be concentrated into the KD flask, and attach a three-ball Snyder column.

Turn on the hot (95°C) water flow to the jacketed concentrator tube.

Concentrate to 1 mL. If the determinative method requires a solvent exchange, add the appropriate exchange solvent (5-10 mL hexane, 1 mL acetonitrile, 4 mL acetone/hexane) to the top of the Snyder column. Continue to concentrate until the Snyder column balls stop chattering.

Cool the jacketed concentrator tube until it is cold to the touch.

Quantitatively transfer the extract and dilute to final volume, or continue concentration with nitrogen evaporation (Section 11.10).

11.11. Turbovap Method

11.11.1. Turn on the Turbovap and adjust the water temperature to 5-10°C less than the boiling point of the solvent to be evaporated.

11.11.2. Switch all endpoint sensors to the correct position.

11.11.3. Adjust the water bath level

11.11.4. Adjust the nitrogen gas pressure to approximately 14 psi.

11.11.5. Transfer the extract into the Turbovap tube and load into the Turbovap. Do not fill the Turbovap tubes over approximately 3/4 full.

11.11.6. Reset the sensor and close the lid.

Note: If the extract splashes when the nitrogen flow starts, reduce the nitrogen flow or transfer a portion of the extract back into the original extract container.

11.11.7 As the extract concentrates, transfer the remainder of the extract into the appropriate Turbovap tube. After all of the extract has been

transferred, rinse the flask with a few mL of methylene chloride and add to the Turbovap tube.

11.11.8. Concentrate the extract to slightly less than the required final volume.

11.11.9. If solvent exchange is required, concentrate to 1-4 mL and add appropriate volume of the exchange solvent. Concentrate back down to the appropriate volume. Refer to Table 2 for details of exchange solvents and final volumes.

11.11.10. Transfer the concentrated extract to volumetric glassware for adjustment of final volume, using a small amount of solvent to rinse the tube and complete the transfer.

Note: Water contamination from condensation during concentration is not acceptable. If water is present, remove the Turbovap tube and filter the extract through sodium sulfate. Transfer to a clean Turbovap tube and continue the concentration.
Note 2: Dark, opaque or turbid samples may not concentrate. If this occurs, supervise the entire concentration procedure.

11.12. Cleanup Techniques

11.12.1. The following techniques may be used to remove interfering peaks, and /or to remove materials that may cause column deterioration and/ or loss of detector sensitivity.

11.12.2. *Gel Permeation Chromatography* (Section 11.13) is a generally applicable technique which can be used to prepare extracts for Semivolatiles (8270), and pesticides (8081) analysis. It is capable of separating high molecular weight material from the sample analytes, and so is particularly useful if tissue or vegetable matter is part of the sample, and for many soil samples. Note: GPC used only for CLP Projects

11.12.3. *Florisil column cleanup* (Section 11.21) is particularly useful for cleanup of pesticides for analysis by method 8081 and should normally be applied to these samples unless the matrix is clean. It separates compounds with a different polarity from the target analytes. Note: GPC used only for CLP Projects. Gel Permeation Chromatography and Florisil column cleanup may both be applied to samples for analysis by method 8081/8082. In this case the GPC should be performed first.

11.12.4. *Sulfur cleanup* (Section 11.23) is generally applied to samples for analysis by method 8081/8082, since the Electron Capture Detector responds strongly to sulfur. It is performed after GPC and Florisil cleanup.

11.12.5. *Sulfuric acid cleanup* (Section 11.24) is applied to samples requiring analysis for Polychlorinated Biphenyls (PCBs) only. Most organic matter is destroyed by the sulfuric acid. WARNING: Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

11.12.6. Acid Base Partition Cleanup (Section 11.25) is useful for separating organic acids and phenols from basic and neutral organics.

11.12.7. Fluorocarbon cleanup (Section 11.26) is used to remove hydrocarbons from water samples to be analyzed for water soluble alcohols.

11.13. Gel Permeation Chromatography (GPC)

Note: GPC system used is J2 Scientific Accuprep.

11.14. GPC Column Preparation

11.14.1. Weigh out 70 g of Bio Beads (SX-3) into a 400-mL beaker.

11.14.2. Add approximately 300 mL of methylene chloride and stir gently.

11.14.3. Cover with aluminum foil and allow the beads to swell for a minimum of two hours. Maintain enough solvent to sufficiently cover the beads at all times.

11.14.4. Position and tighten the outlet bed support (top) plunger assembly in the tube by inserting the plunger and turning it clockwise until snug. Install the plunger near the column end but no closer than 5 cm (measured from the gel packing to the collar).

11.14.5. Turn the column upside down from its normal position with the open end up. Place the tubing from the top plunger assembly into a waste beaker below the column.

11.14.6. Swirl the bead/solvent slurry to get a homogeneous mixture and pour the mixture into the open end of the column. Transfer as much as possible with one continuous pour trying to minimize bubble formation. Pour enough to fill the column. Wait for the excess solvent to drain out before pouring in the rest. Add additional

methylene chloride to transfer the remaining beads and to rinse the beaker and the sides of the column. If the top of the gel begins to look dry, add more methylene chloride to rewet the beads.

11.14.7. Wipe any remaining beads and solvent from the inner walls of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

> **CAUTION**: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

11.14.8. Push the plunger until it meets the gel, then compress the column bed about 4 cm.

11.14.9. Connect the column inlet to the solvent reservoir and place the column outlet tube in a waste container. Pump methylene chloride through the column at a rate of 5 mL/min. for one hour.

11.14.10. After washing the column for at least one hour, connect the column outlet tube to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. Placing a restrictor (made from a piece of capillary tubing of 1/16"OD x 10/1000"ID x 2") in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect the flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi back-pressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

11.14.11. When the GPC column is not to be used for several days, connect the column inlet and outlet lines to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, pump methylene chloride through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify that retention volumes have not changed.

11.15. Initial Calibration of the GPC Column

11.15.1. Before use, the GPC must be calibrated based on monitoring the elution of standards with a UV detector connected to the GPC column.

11.15.2. Pump solvent through the GPC column for 2 hours. Verify that the flow rate is 4.5-5.5 mL/min. Corrective action must be taken if the flow rate is outside this range. Record the column pressure (should be 6-10 psi) and room temperature (22°C is ideal).

Note: Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared.

11.15.3. Inject the calibration solution and retain a UV trace that meets the following requirements (See resolution calculation in Section 11.20.1.):

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

11.15.4. A UV trace that does not meet the criteria in Section 11.15.1. indicates the need for system maintenance and/or the need for a new column.

11.15.5. Determine appropriate collect and dump cycles.

11.15.6. The calibrated GPC program for pesticides/PCB should dump >85% of the phthalate and should collect >95% of the methoxychlor and perylene. Use a wash time of 10 minutes.

11.15.7. For semivolatile extracts, initiate a column eluate collection just before the elution of bis (2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a wash time of 10 minutes after the elution of sulfur.

11.15.8. Reinject the calibration solution after appropriate dump and collect cycles have been set.

11.15.9. Measure and record the volume of collected GPC eluate in a graduated cylinder.

11.15.10. The retention times for both bis(2-ethylhexyl) phthalate and perylene must not vary more than +/- 5% between calibrations.

11.16. GPC calibration check

11.16.1. Check the calibration of the GPC immediately after the initial calibration and at least every 7 days thereafter, while the column is in use.

11.16.2. Inject the calibration solution, and obtain a UV trace. If the retention times of bis(2-ethylhexyl)phthalate or perylene have changed by more than ± 5% use this run as the start of a new initial calibration. Otherwise, proceed with the recovery check. Excessive retention time shifts may be caused by poor laboratory temperature control or system leaks, an unstabilized column, or high laboratory temperature causing outgassing of methylene chloride. Pump methylene chloride through the system and check the retention times each day until stabilized.

11.17. GPC Recovery Check for Pesticides/ PCBs

11.17.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Two recovery check solutions are used. The first mixture is prepared by diluting 1.0 2.0 mL of the pesticide matrix spiking solution (Table 6) to 10 mL in methylene chloride. The second mixture is prepared by diluting 12.0 mL of the PCB only matrix spiking solution (Table 6) to 10 mL with methylene chloride.

11.17.2. Load the pesticide matrix spike mixture, the PCB mixture, and a methylene chloride blank onto the GPC using the GC dump and collect values.

Note: If the analysis is for PCBs only, then the pesticide recovery check is not necessary.

11.17.3. After collecting the GPC calibration check fraction, concentrate, solvent exchanging to hexane. Adjust the final volume to 5.0 mL, and analyze by GC/EC. Refer to concentration, Section 11.9.

11.17.4. The methylene chloride blank may not exceed more than one half the reporting limit of any analyte. And if the recovery of each of the single component analytes is 80-10120% and if the Aroclor pattern is the same as previously run standards, then the analyst may use the column. If the above criteria are not met, there may be a need for system maintenance.

11.18. GPC Blank for Semivolatiles

11.18.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use.

11.18.2. Load a methylene chloride blank onto the GPC using the semivolatiles dump and collect values.

11.18.3. After collecting the GPC recovery check fraction, concentrate, and analyze by GC/MS. Refer to the concentration Section 11.9.

The blank should not contain any analytes at or above the reporting limit. If these conditions are met the column may be used for sample analysis. Otherwise correct the contamination problem, or extend the collect time to improve recovery of target analytes.

11.19. Sample Extract Cleanup

11.19.1. Reduce the sample extract volume to 1-2 mL, then adjust to 10 mL with methylene chloride prior to cleanup. This reduces the amount of acetone in the extract. Refer to Section 11.9.

11.19.2. Start the pump and let the flow stabilize for 2 hours. The solvent flow rate should be 4.5-5.5 mL/min. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C. The normal backpressure is 6-10 psi.

11.19.3. In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution (by visual comparison) must be diluted and loaded into several loops.

11.19.4. Samples being loaded onto the GPC should be filtered with a 5 micron (or less) filter disk. Attach a filter to a 10 mL Luerlok syringe and filter the 10 mL sample extract into the sample tube.

11.19.5. Load the filtered samples into the proper sample tubes and place on the GPC.

11.19.6. Set the collect, dump, and wash times determined by the calibration procedure.

11.19.7. Switch to the run mode and start the automated sequence. Process each sample using the collect and dump cycle times established by the calibration procedure.

11.19.8 Collect each sample in a suitable glass container. Monitor sample volumes collected.

11.19.9. Any samples that were loaded into 2 or more positions must be recombined.

11.19.10. Concentrate semivolatile sample extracts to 0.5 mL in methylene chloride. Refer to the concentration Section 11.9.

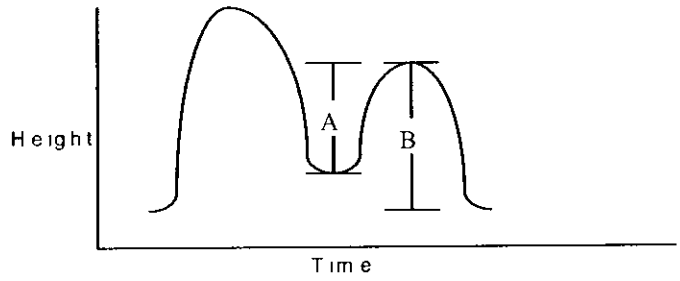
11.19.11. Solvent exchange pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL. Refer to the concentration Section 11.9.

11.20. Calculations

11.20.1. Resolution

To calculate the resolution between two peaks on a chromatograph, divide the depth of the valley between the peaks by the peak height of the smaller peak being resolved and multiply by 100.

Resolution Calculation



$$\% \text{ Resolution} = \frac{A}{B} \times 100$$

Where: A = depth of valley to height of smaller peak
B = peak height of smaller peak

11.20.2. Dump Time

Mark on the chromatograph the point where collection is to begin. Measure the distance from the injection point. Divide the distance by the chart speed. Alternatively the collect and dump times may be measured by means of an integrator or data system.

$$\text{Dump time (min)} = \frac{\text{Distance (cm) from injection to collection start}}{\text{Chart speed (cm / min)}}$$

11.20.3. Collection Time

$$\text{Collection time (min)} = \frac{\text{Distance (cm) between collection start and stop}}{\text{Chart speed (cm / min)}}$$

11.21. Florisil Cartridge Cleanup

Florisil cleanup is generally used for organochlorine pesticides, although it may be applied to other analytes. Sections 11.21.1 through 11.21.8 outline the procedure for organochlorine pesticides, while section 11.22 outlines modifications required for other analytes.

Note 1: Systems for eluting multiple cleanup cartridges include the Supelco, Inc. Solid Phase Extraction (SPE) assembly or equivalent.

Note 2: Follow the lab specific procedure when using ABC Model 1002B.

11.21.1. Before Florisil cleanup sample volume must be reduced to 10 mL (5 mL if GPC cleanup was used) and the solvent must be hexane. Refer to Section 11.9 for details of concentration.

11.21.2. Attach a vacuum manifold to a vacuum pump or water aspirator with a trap installed between the manifold and the vacuum. Adjust the vacuum in the manifold to 5-10 psi.

11.21.3. Place one Florisil cartridge into the vacuum manifold for each sample extract. Prior to cleanup of samples, pre-elute each cartridge with 5 mL of hexane/acetone (9:1). Adjust the vacuum applied to each cartridge so that the flow through each cartridge is approximately 2 mL/min. Do not allow the cartridges to go dry.

11.21.4. Just before the cartridges go dry, release the vacuum to the manifold and remove the manifold top.

11.21.5. Place a rack of clean labeled 12 mL concentrator tubes into the manifold and replace the manifold top. Make sure that the solvent line from each cartridge is placed inside the appropriate tube.

11.21.6. After the clean tubes are in place, vacuum to the manifold is restored and 2.0 mL of the extract is added to the appropriate Florisil cartridge.

11.21.7. The pesticides/aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL culture tube or concentrator tube held in the rack inside the vacuum manifold.

11.21.8. Transfer the extract to a graduated concentrator tube and concentrate the extract to 2 mL. Refer to the concentration Section. (11.9)

Note 1: A cartridge performance standard must be run with each lot of Florisil cartridges.

Note 2: Florisil cartridge performance check--every lot number of Florisil must be tested before use. Add 0.5 ug/mL of 2,4,5-trichlorophenol solution and 0.5 mL of GC Standard Mix A (midpoint concentration) to 4 mL hexane. Reduce volume to 0.5 mL. Add the concentrate to a pre-washed Florisil cartridge and elute with 9 mL hexane/acetone [(90:10)(v/v)]. Rinse cartridge with 1.0 mL hexane two additional times. Concentrate eluate to 1.0 mL final volume and transfer to vial. Analyze the solution by GC/EC. The test sample

must show 80 to 120% recovery of all pesticide analytes with <5% trichlorophenol recovery, and no peaks interfering with target compounds can be detected. This standard has a lifetime of six months. Alternatively, this standard may be purchased as a stock solution.

11.22. Modifications for other analyte classes

11.22.1.PCBs

Pre-elute the cartridge with 4 mL hexane. Add 2 mL of the sample extract and elute with 3 mL hexane. The eluant will contain the PCBs together with any heptachlor, aldrin, 4,4'DDE and part of any 4,4'DDT. Any BHC isomers, heptachlor epoxide, chlordane, endosulfan I and II, endrin aldehyde and endrin sulfate and methoxychlor will be retained on the column and can be eluted in a separate fraction with 8 mL 90:10 hexane:acetone if required.

11.23. Sulfur Removal

11.23.1. Sulfur can be removed by one of three methods: mercury, copper, or tetrabutylammonium sulfite (TBA) according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipet, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

11.23.2. Sulfur Removal with Elemental Mercury

Note: Use Mercury sparingly in order to minimize exposure and disposal costs.

11.23.2.1. Transfer 2 mL of sample extract into a clean concentrator tube or Teflon sealed vial.

11.23.2.2. Add one to three drops of mercury to the extract vial and seal.

11.23.2.3. Shake well for 15-30 seconds. If prolonged shaking is required, use a mechanical shaker.

11.23.2.4. Remove the extract from the mercury using a disposable pipette and transfer to a clean vial.

11.23.2.5. If black precipitate forms, sulfur was present. Shake again, then centrifuge. After centrifugation, transfer the supernate to a clean test tube and repeat. Do this until relatively little

precipitate remains, or the screens indicate that cleanup is complete.

11.23.2.6. Properly dispose of the mercury waste.

11.23.3. Sulfur Removal with Copper

11.23.3.1. Transfer 1.0 mL of sample extract into a centrifuge or concentrator tube.

11.23.3.2. Add approximately 2 g of cleaned copper powder (see Section 7.2 for copper cleaning procedure) to the sample extract tube.

11.23.3.3. Mix for one minute on a mechanical shaker.

11.23.3.4. If the copper changes color, sulfur was present. Repeat the sulfur removal procedure until the copper remains shiny.

11.23.3.5. Transfer the supernate to a clean vial.

11.23.4. Sulfur Removal with Tetrabutylammonium (TBA) Sulfite Reagent

11.23.4.1. Transfer 1.0 mL of sample extract into a culture tube.

11.23.4.2. Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol to the sample extract. Cap and shake for 1 minute. If clear crystals (precipitated sodium sulfite) form, sufficient sodium sulfite is present.

11.23.4.3. If a precipitate does not form, add sodium sulfite in an approximately 0.1 g portions until a solid residue remains after repeated shaking.

11.23.4.4. Add 5 mL organic free reagent water and shake for 1 minute. Allow sample to stand for 5-10 minutes. (Centrifuge if necessary to separate the layers). Transfer the sample extract (top layer) to a vial. The final volume is defined as 1.0 mL in Section 11.23.4.1.

11.24. Sulfuric Acid Cleanup

11.24.1. Add approximately 2-5 mL of concentrated sulfuric acid to 2 mL of sample extract in a Teflon capped vial.

Caution: There must be no water present in the extract or the reaction may shatter the sample container.

11.24.2. Shake or vortex for about thirty seconds and allow to settle. (Centrifuge if necessary)

11.24.3. Remove the sample extract (top layer) from the acid using a Pasteur pipette and transfer to a clean vial. ***CAUTION:*** It is not necessary to remove all the extract since the final volume is already determined. Transfer of small amounts of sulfuric acid along with the extract will result in extremely rapid degradation of the chromatographic column.

11.24.4. If the sulfuric acid layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until color is no longer being removed by the acid, or a maximum of 5 acid cleanups.

11.24.5. Properly dispose of the acid waste.

11.25. Acid/Base Partition Cleanup

11.25.1. Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL separatory funnel.

11.25.2. Add 20 mL of methylene chloride to the separatory funnel.

11.25.3. Slowly add 20 mL of DI water which has been previously adjusted to a pH of 12 to 13 with 10 N sodium hydroxide.

11.25.4. Seal and shake the separatory funnel for at least two minutes with periodic venting to release excess pressure.

CAUTION: Methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the separatory funnel has been sealed.

11.25.5. Allow the organic layer to separate from the aqueous phase for a minimum of ten minutes.

11.25.6. If an emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

11.25.7. Separate the aqueous phase and transfer it to a 125 mL Erlenmeyer flask. Repeat the extraction two more times using fresh 20 mL aliquots of dilute sodium hydroxide (pH 12-13) . Combine the aqueous extracts.

11.25.8. Water-soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase discard the methylene chloride and proceed to Section 11.25.9. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to Section 11.25.11.

11.25.9. Externally cool the flask with ice while adjusting the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Transfer the cool aqueous phase to a clean 125 mL separatory funnel.

11.25.10. Add 20 mL of methylene chloride to the separatory funnel and shake for at least two minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask. Repeat the extraction two more times using fresh methylene chloride and extracting at pH 1-2. Combine the three extracts.

11.25.11. Dry the extract by passing through a funnel containing 10-20 g anhydrous sodium sulfate. Rinse the funnel with an additional 20-30 mL of clean methylene chloride

11.25.12. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.9 for concentration.

11.25.13. Dispose of solvent and water remaining in the separatory funnel into the appropriate waste container.

11.26. Fluorocarbon Cleanup

This procedure is appropriate for the removal hydrocarbons from water samples prior to analysis for water soluble alcohols

11.26.1. Transfer 1-2 mL of water sample to a 10 mL culture tube.

11.26.2. Add 1-2 mL of fluorocarbon solvent (PF-5080) to the culture and cap.

11.26.3. Shake for 30-60 seconds.

11.26.4. After the two phases have separated, pipette about 1 mL of water sample (top layer) into an autosampler vial for analysis. If necessary, centrifuge to enhance the phase separation.

12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The procedure for the determination of the method detection limit is given in STL North Canton QA Policy #: QA-005

13.2. Initial Demonstration

Each laboratory must make an initial demonstration of capability for each individual method. This requires analysis of four QC Check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The spiking level should be equivalent to a mid-level calibration. (For certain tests more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.2.2. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. (CORP-GC-0001, CORP-MS-0001, 0002)

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this method is carried out.

15.2.1. **Extracted aqueous samples contaminated with methylene chloride.** Samples are drained into the liquid-liquid separation unit located in extractions. This tank is then periodically rolled to the tank room where the DCM is emptied a larger tank using tubing attached to the bottom of the tank. The remaining water is neutralized with sodium bicarbonate, the pH verified and the water discharged to the sanitary sewer. The waste is disposed of as Methylene chloride contaminated waste.

15.2.2. Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride/acetone or acetone/hexane from the extract drying step. These materials are disposed of in the solid waste and debris in a red container located in the extractions lab.

15.2.3. **Assorted flammable solvent waste from various rinses**. These wastes are put into the halogenated/non-halogenated 25 gallon solvent waste container located under the fume hood in extractions.

15.2.4. **Methylene chloride waste from various rinses:** These wastes are disposed of in the liquid-liquid separation unit.

15.2.5. **Hexane- Hexane waste:** These samples are to be disposed in the flammable waste.

15.2.6. **Waste Hexane in vials.** These vials are placed in the vial waste located in the GC prep laboratory.

15.2.7. **Waste Methylene Chloride sample vials**. These vials are placed in the vial waste located in the GC prep laboratory.

15.2.8. **Extracted solid samples contaminated with methylene chloride/acetone or acetone/hexane.** These materials are disposed of in the solid waste and debris in a red container located in the extractions lab.

15.2.9. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCB's must be segregated into their own waste stream.

PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB and PCB vial waste.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3510C, 3520C, 3540C, 3550B, 3600C, 3610B, 3620B, 3640A, 3650B, 3660B, AND 3665A.

16.1.2. Corporate Quality Management Plan (QMP), current version.

16.1.3. STL Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003
16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

16.2.6. Hazardous Waste Management SOP, NC-HS-0001.

17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Aqueous sample volumes may be determined by weight.

17.1.3. Spiking levels for method 608 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

17.1.4. 10 g of soil is used for pH determination, rather than the 50 g suggested in the reference method. The volume of water is also adjusted to maintain the sample / water ratio specified in the method.

17.2. Modifications from previous revision

17.2.1. SOP change forms are on record in the Quality Assurance Department.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.3. Tables

Table 1
Liquid /Liquid Extraction Conditions

Determinative Method	Initial Ext. pH	Secondary Ext. pH
BNA: 8270C[1]	1-2	11-12
625	11-12	1-2
Pest/PCB: 8081A, 8082 & 608	5-9	None
Wisconsin DRO	2	
OPP: 8141A	as received	None
Hydrocarbons: 8015B	as received	None
PAH: 8310, & 610	as received	None

[1] If the laboratory has validated acid only 8270 extraction for the target compound list required then the base extraction step may be omitted. The required validation consists of a 4 replicate initial demonstration of capability and a method detection limit study. (See section 13). Additionally, either of the base or acid fractions of Method 8270 can be run first.

Table 2
Exchange Solvents and Final Volumes

Final Volumes and Exchange Solvents if no cleanup is used		
Type	Exchange Solvent for Analysis	Final Volume for Analysis in mL
Semivolatiles	N/A	2.0 mL
PCB	50mL Hexane	10.0 for solids 5.0 for H2O 2.0 for H2O**
Pesticides	50mL Hexane	10.0 for solids 5.0 for H2O
Pesticides/TCLP	50mL Hexane	3.0 mL
PAH by HPLC	4mL Acetonitrile	1.0 mL
BNA – SIM	N/A	2.0 mL - Solids & H2O
TPH	N/A	1.0
OPP	20mL Hexane/Acetone	2.0

*Requires high sensitivity mass spec tune (refer to NC-MS-0015 PAH by SIM)
** Michigan work requires a final volume of 2 mL.

Final Volumes and solvents if GPC cleanup is used CLP ONLY – SOLIDS ONLY			
Type	Solvent for GPC	Final Volume for GPC	Final Volume and solvent for Analysis
Semivolatiles	CH_2Cl_2	10 mL[1]	0.5 mL CH_2Cl_2 - OLM03.1
Semivolatiles	CH_2Cl_2	10 mL[1]	2.5 mL CH_2Cl_2 - OLM04.2
Pesticides	CH_2Cl_2	10 mL[1]	5 mL, Hexane

[1] Final volume for GPC may be 4 mL if a 2 mL sample loop is used

Final volumes and solvents if Florisil cleanup is used CLP ONLY			
Type	Solvent for Florisil	Final Volume for Florisil	Final Volume and solvent for Analysis
Pesticides	Hexane	10 mL (2 mL aliquot used)	2 mL, hexane

Final volumes and solvents if both GPC and Florisil cleanup are used CLP ONLY					
Type	Solvent for GPC	Final Volume for GPC	Solvent for Florisil	Final Volume for Florisil	Final volume for analysis
Pesticides	Methylene Chloride	10 mL	Hexane	5 mL (2 mL aliquot used)	2 mL, hexane

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

.Table 3
Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA	100/150 ppm BNA	0.2
BNA / SIM	100/150 ppm BNA	.2 / 0.02
PEST	0.2 ppm DCB/TCX	1.0
TPH	40ng C9	1.0
PCB	0.2 ppm DCB/TCX	1.0
PAH	1.0 ug/mL p-Terphenyl-d14 5.0 ug/mL Benzo(e)pyrene	1.0
OPP	10 ug/mL Triphenyl Phosphate	1.0

Table 4

Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
BNA	100 ppm BNA All-Analyte Spike & Restek Spike	0.2
BNA / SIM	100 ppm BNA All-Analyte Spike & Restek Spike	0.2 / 0.02
PEST	Pest NPDES Spike	1.0
PEST TCLP	Pest TCLP Spike	1.0
PCB	10 ppm PCB Spike	1.0
PAH	See Spike List – Table 6	1.0
TPH	See Spike List – Table 6	1.0
OPP	See Spike List – Table 6	1.0

Table 5
Surrogate Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
BNA	2-Fluorobiphenyl	Methanol	100
	Nitrobenzene-d5		100
	p-Terphenyl-d14		100
	2-Fluorophenol		150
	Phenol-d6		150
	2,4,6-Tribromophenol		150
	1,2-Dichlorobenzene-d4		100
	2-Chlorophenol-d4		150
Pest/PCB	Decachlorobiphenyl	Methanol Acetone	0.2
	Tetrachloro-m-xylene		0.2
TPH	Nonane (C9)	Methanol	40.0
PAH	p-Terphenyl-d-14	CH3CN	1.0
	Benzo(e)pyrene		5.0
OPP	Triphenylphosphate	Acetone	10.0

Table 6
Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
TCL BNA	Acenaphthene	Methanol	100
	4-Chloro-3-Methylphenol		150
	2-Chlorophenol		150
	1,4-Dichlorobenzene		100
	2,4-Dinitrotoluene		100
	4-Nitrophenol		150

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	N-Nitroso-Di-n-Propylamine		100
	Pentachlorophenol		150
	Phenol		150
	Pyrene		100
	1,2,4-Trichlorobenzene		100
BNA TCLP	1,4-Dichlorobenzene	Methanol	100
	2,4-Dinitrotoluene		100
	Hexachlorobenzene		100
	Hexachlorobutadiene		100
	Hexachloroethane		100
	2-Methylphenol		100
	3-Methylphenol		100
	4-Methylphenol		100
	Nitrobenzene		100
	Pentachlorophenol		100
	Pyridine		100
	2,4,5-Trichlorophenol		100
	2,4,6-Trichlorophenol		100
BNA NPDES		Methanol	
	Acenaphthene		100
	Acenaphthylene		100
	Anthracene		100
	Benzo(a)anthracene		100
	Benzo(b)fluoranthene	Methanol	100

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Benzo(k)fluoranthene		100
	Benzo(a)pyrene		100
	Benzo(ghi)perylene		100
	Benzyl butyl phthalate		100
	Bis(2-chloroethyl)ether		100
	Bis(2-chloroethoxy)methane		100
	Bis(2-ethylhexyl)phthalate		100
	Bis(2-chloroisopropyl)ether		100
	4-Bromophenyl phenyl ether		100
	2-Chloronaphthalene		100
	4-Chlorophenyl phenyl ether		100
	Chrysene		100
	Dibenzo(a,h)anthracene		100
	Di-n-butylphthalate		100
	1,3-Dichlorobenzene		100
	1,2-Dichlorobenzene		100
	1,4-Dichlorobenzene		100
	3,3'-Dichlorobenzidine		100
	Diethyl phthalate		100
	Dimethyl phthalate		100
	2,4-Dinitrotoluene		100
	2,6-Dinitrotoluene		100
	Di-n-octylphthalate		100
	Fluoranthene		100
	Fluorene		100

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Hexachlorobenzene		100
	Hexachlorobutadiene		100
	Hexachloroethane		100
	Indeno(1,2,3-cd)pyrene		100
	Isophorone		100
	Naphthalene		100
	Nitrobenzene		100
	N-Nitrosodi-n-propylamine		100
	Phenanthrene		100
	Pyrene		100
	1,2,4-Trichlorobenzene		100
	4-Chloro-3-methylphenol		100
	2-Chlorophenol		100
	2,4-Dichlorophenol		100
	2,4-Dimethylphenol		100
	2,4-Dinitrophenol		100
	2-Methyl-4,6-dinitrophenol		100
	2-Nitrophenol		100
	4-Nitrophenol		100
	Pentachlorophenol		100
	Phenol		100
	2,4,6-Trichlorophenol		100
	Acetophenone		100
	Atrazine		100
	Caprolactum		100

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Benzaldehyde		100
	1,1′-Biphenyl		100
	Safrole		100
	1,4-Dioxane		100
	Pronamide		100
	p-Chlorobenzilate		100
	Phenacetin		100
	Ethyl methanesulfonate		100
	2-Picoline		100
	Phorate		100
	Quinoline		100
Pest TCLP	Heptachlor	Methanol Acetone	0.5
	Heptachlor epoxide		0.5
	Lindane		0.5
	Endrin		0.5
	Methoxychlor		1.0
Pest NPDES /Pest	Aldrin	Methanol Acetone	1.0
	alpha-BHC		1.0
	beta-BHC		1.0
	delta-BHC		1.0
	gamma-BHC (Lindane)		1.0
	4,4'-DDD		1.0
	4,4'-DDE		1.0

Table 6			
Matrix Spike Components			
Type	Compounds	Solvent	Conc. (µg/mL)
	4,4'-DDT		1.0
	Dieldrin		1.0
	alpha-Endosulfan		1.0
	beta-Endosulfan		1.0
	Endosulfan Sulfate		1.0
	Endrin		1.0
	Heptachlor		1.0
	Heptachlor Epoxide		1.0

Diesel Range Organics (8015B) Spike	
Compound	**Final Concentration**
n-decane	50 µg/ml
n-dodecane	50 µg/ml
n-tetradecane	50 µg/ml
n-hexadecane	50 µg/ml
n-octadecane	50 µg/ml
n-eicosane	50 µg/ml
n-docosane	50 µg/ml
n-tetracosane	50 µg/ml
n-hexacosane	50 µg/ml
n-octacosane	50 µg/ml

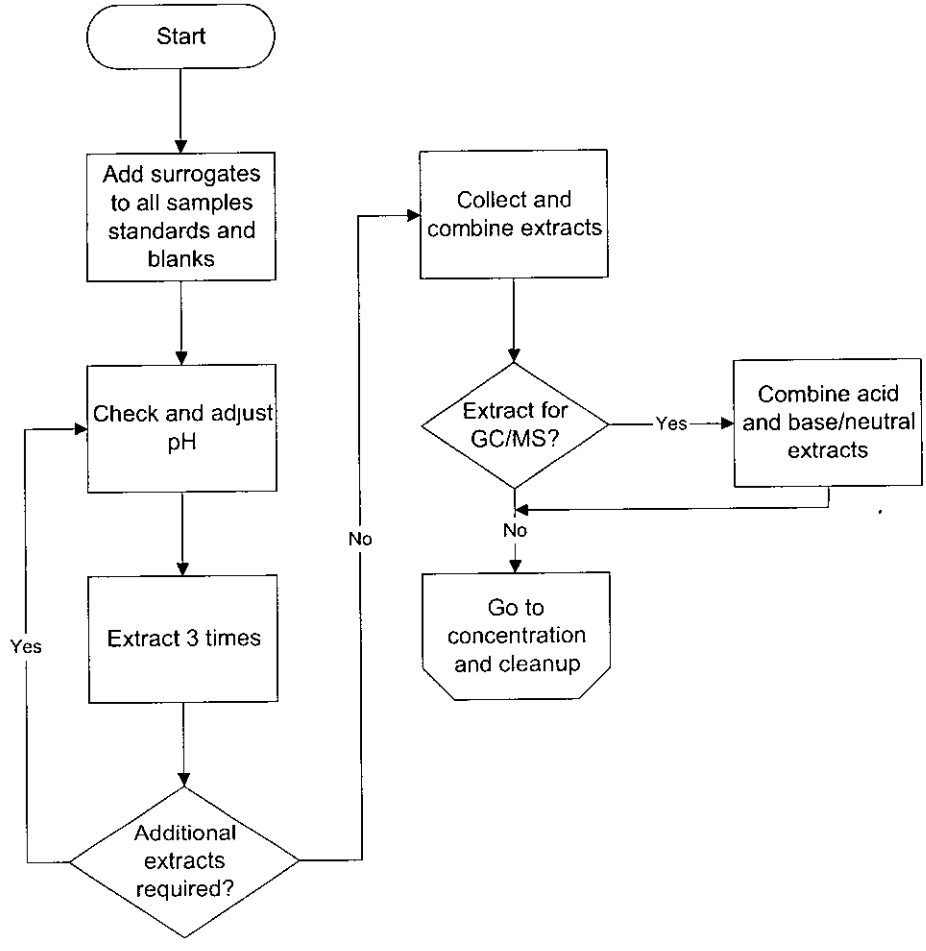
Organophorphorous Pesticides (8141A)	
Compound	**Final Concentration**
dimethoate	20 µg/mL
disulfoton	20 µg/mL
famphur	20 µg/mL
methyl parathion	20 µg/mL

parathion (ethyl)	20 µg/mL
phorate	20 µg/mL
sulfotepp	20 µg/mL
thionazin	20 µg/mL
o,o,o-triethyl phosphorothioate	20 µg/mL
triphenylphosphate (surrogate)	20 µg/mL

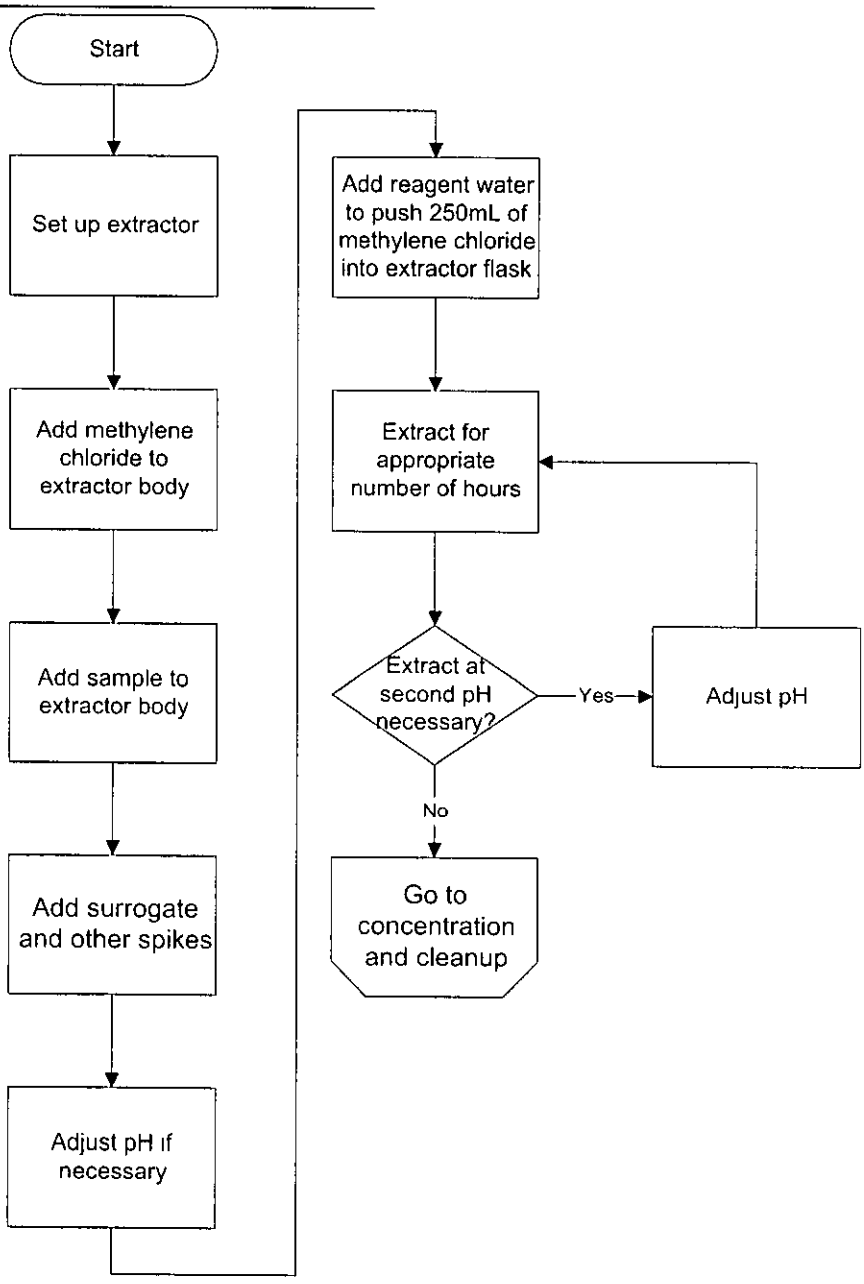
Polynuclear Aromatic Hydrocarbons (8310)	
Compound	**Final Concentration**
Acenaphthylene	10 µg/mL
Carbazole	10 µg/mL
Naphthalene	10 µg/mL
1-Methylnaphthalene	10 µg/mL
2-Methylnaphthalene	10 µg/mL
Acenaphthene	10 µg/mL
Fluorene	2 µg/mL
Phenanthrene	2 µg/mL
Anthracene	2 µg/mL
Fluoranthene	2 µg/mL
Pyrene	2 µg/mL
Benzo(a)anthracene	2 µg/mL
Chrysene	2 µg/mL
Benzo(a)pyrene	2 µg/mL
Benzo(k)fluoranthene	2 µg/mL
Benzo(a)pyrenek)fluoranthene	2 µg/mL
Dibenzo(a,h)anthracene	2 µg/mL
Benzo(g,h,I)perylene	2 µg/mL
Indeno(1,2,3-cd)pyrene	2 µg/mL

17.5. Flow diagrams

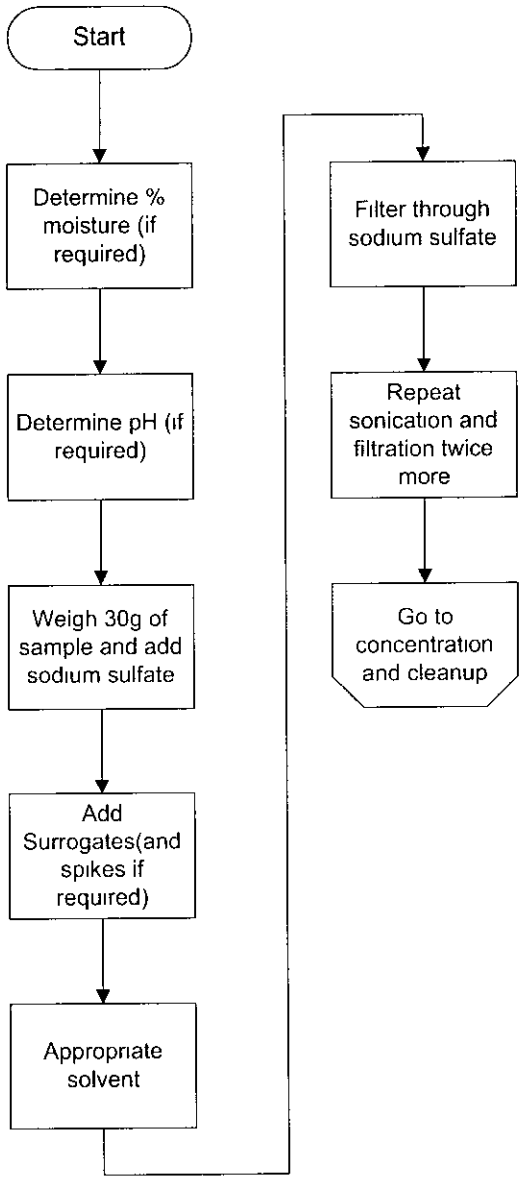
17.5.1. Separatory funnel extraction



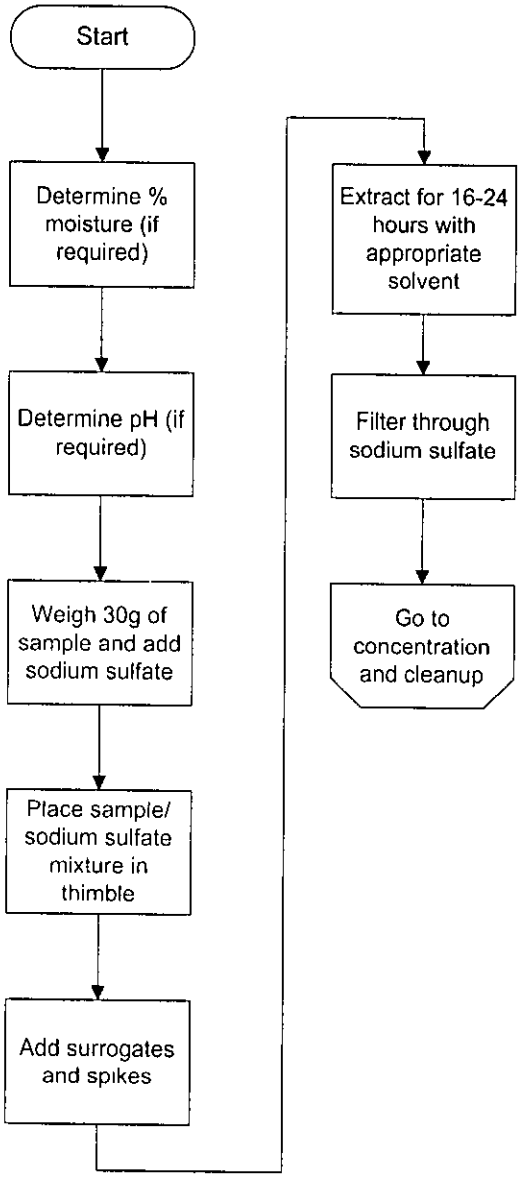
17.5.2. Continuous liquid/liquid extraction


Start
Set up extractor
Add methylene chloride to extractor body
Add sample to extractor body
Add surrogate and other spikes
Adjust pH if necessary
Add reagent water to push 250mL of methylene chloride into extractor flask
Extract for appropriate number of hours
Extract at second pH necessary?
Yes
Adjust pH
No
Go to concentration and cleanup

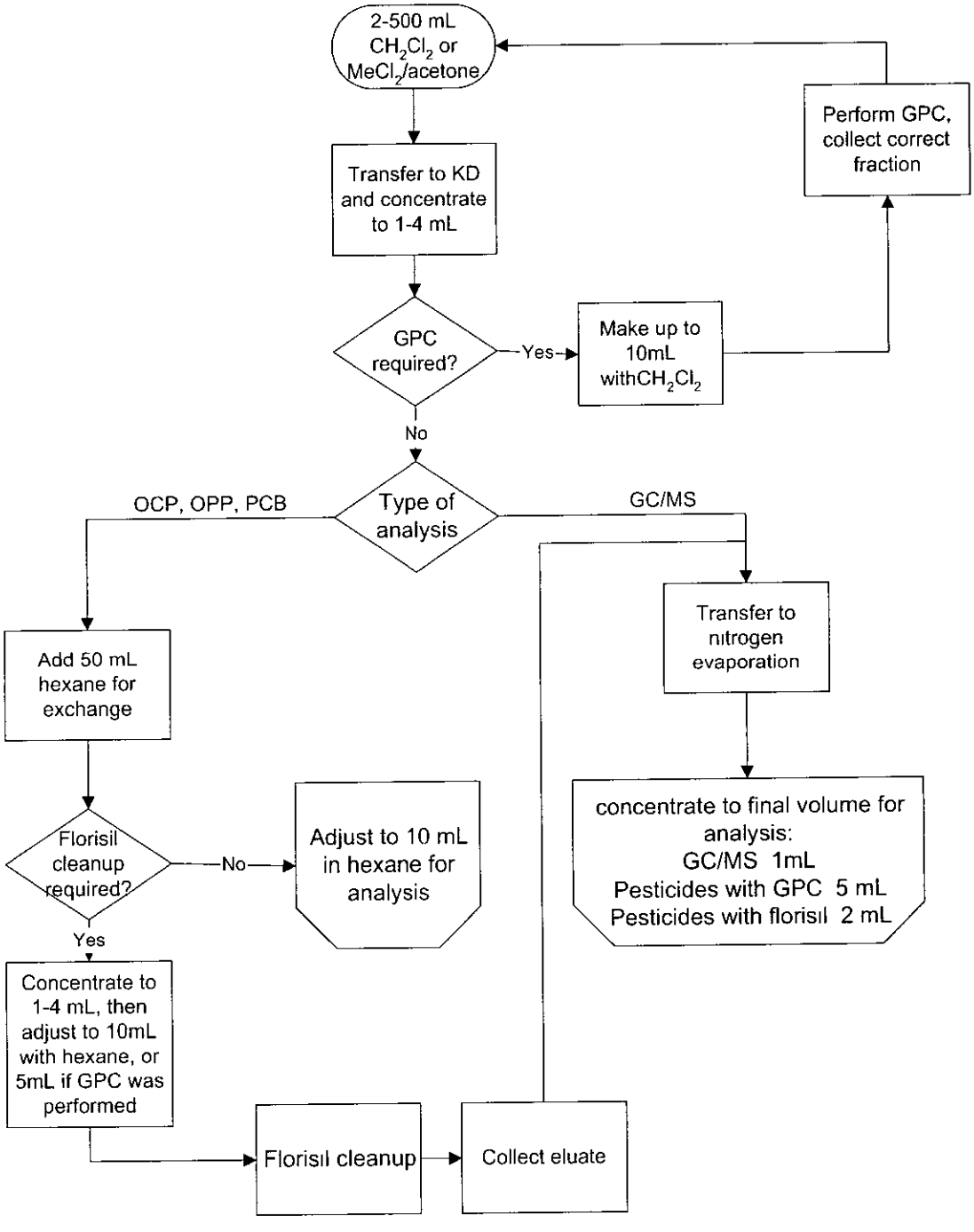
17.5.3. Sonication Extraction



17.5.4. Soxhlet extraction



17.5.5. Concentration and cleanup



1. SCOPE AND APPLICATION

1.1. This method is applicable to the extraction of chlorinated herbicides in waters, solids, oils, and TCLP extracts. Appropriate compounds for extraction by this method are listed in CORP-GC-0001, Appendix D, Gas Chromatography of Phenoxy Acid Herbicides based on Method 8151A.

2. SUMMARY OF METHOD

2.1. This method is based on SW846 method 8151A. Aqueous samples are hydrolyzed if esters and acids are to be determined, then washed with methylene chloride by a separatory funnel extraction. After acidifying the sample the free acids are extracted into diethyl ether. Solids are extracted into methylene chloride/ acetone by sonication. If esters and acids are to be determined, the extract is hydrolyzed and extracted into diethyl ether. For both soils and aqueous samples, the free acid herbicides in the ether extract are esterified. The final volume is adjusted to prepare the extract for gas chromatography.

3. DEFINITIONS

3.1. Refer to section 3 of the main body of this SOP.

4. INTERFERENCES

4.1. Refer to section 4 of the main body of this SOP.

5. SAFETY

5.1. Refer to section 5 of the main body this SOP for basic safety information.

5.2. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free of scratches, cracks, chips and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.

5.3. Diethyl ether must be free of peroxides as demonstrated by EM (or equivalent) Quant test strips. This test can be done every time the ether is used or once per week if the bottle is marked with the test date(s).

5.4. Concentrated potassium hydroxide solution is highly caustic.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure

Nitric Acid	Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Ethyl Ether	Flammable Irritant Peroxide Former	400 ppm-TWA	General anesthesia by inhalation can occur. Continued exposure may lead to respiratory failure or death. Early symptoms include irritation of nose and throat, vomiting, and irregular respiration, followed by dizziness, drowsiness, and unconsciousness. May cause irritation, redness and pain to the eyes. Irritating to the skin and mucous membranes by drying effect. Can cause dermatitis on prolonged exposure. May be absorbed through skin. **May form explosive peroxides on long standing or after exposure to air or light. This material must be disposed of within six months.**
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the main body of this SOP for basic extraction equipment and supplies. Additional equipment and supplies needed for this procedure are listed below.

6.2. Diazomethane generation apparatus

7. REAGENTS AND STANDARDS

7.1. Reagents are listed in Section 7 of the main body of this SOP. Additional reagents and standards needed for this procedure are listed below.

7.2. Reagents

7.2.1. Potassium hydroxide solution, 37% aqueous solution, (w/v): Dissolve 37 g of potassium hydroxide pellets in reagent water and dilute to 100 mL. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

7.2.2. Toluene, reagent grade

7.2.3. 2-(2-Ethoxyethoxy)ethanol, trade name Carbitol, 98%+purity

7.2.4. Diazald, 99% purity

7.2.5. Sodium sulfate, Na_2SO_4, Anhydrous, granular, acidified: Heat sodium sulfate in a shallow tray at 400°C for a minimum of 4 hours to remove phthalates and other interfering organic substances. In a large beaker, acidify by slurrying 500 g sodium sulfate with just enough diethyl ether to cover. Add 20 mL of concentrated sulfuric acid and mix thoroughly. Place the mixture on a steam bath in a hood to evaporate the ether, or allow the ether to evaporate overnight. Larger or smaller batches of acidified sodium sulfate may be prepared using the reagents in the same proportions.

7.2.6. Sodium Chloride, NaCl

7.2.7. BF3-Methanol, Boron trifluoride-MeOH, lab use only

7.2.8. Diethyl ether, reagent grade.

7.2.9. Trimethylsilydiaomethane

7.2.10. Methanol, reagent grade.

7.2.11. Silica gel

7.2.12. 2% methanolic KOH, semi-conductor grade

7.3. Standards

7.3.1. Surrogate Standard

7.3.1.1. See Table A3.

7.3.2. Matrix Spike and LCS standard

7.3.3. See Table A4.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Sample collection and storage is described in Section 8 of the main body of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the main body of this SOP for Quality control procedures.

10. CALIBRATION AND STANDARDIZATION

10.1. Not applicable

11. PROCEDURE

11.1. Preparation of Aqueous Samples

11.1.1. Weigh the sample bottle and pour approximately 500 ml (100 mL for TCLP leachates) into a 1 liter wide-mouth amber jar. Reweigh the bottle and record the sample volume on the benchsheet, assuming a density of 1.0. Alternatively, measure 500 ml in a graduated cylinder. If less than 500 mL was used, reagent water may be added to make the volume up to 500 mL. Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

11.1.2. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2)

11.1.3. Add 60-80 g of NaCl to the sample and shake to dissolve the salt.

11.1.4. Hydrolysis

11.1.4.1. Use this step only if herbicide esters in addition to herbicide acids are to be determined. This is normally the case. If the herbicide esters are not to be determined, omit this step and go to 11.4.1.8.

11.1.4.2. Add 3 mL of 10N NaOH to the sample, seal and shake. Check the pH of the sample with pH paper. If the pH of the sample is not $\geq$12 adjust to $\geq$12 by adding more NaOH. Let the sample sit at room temperature for 2 hours to complete the hydrolysis.

11.1.4.3. Add 300 mL of methylene chloride to the amber jar.

11.1.4.4. Prior to placing samples in tumbler, the samples should be shaken or rotated vigorously for 2 minutes, venting as necessary. Place the samples in tumbler and allow them to tumble for one (1) hour. Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

11.1.4.5. Pour contents of amber jar into a pre-rinsed teflon sep funnel.

11.1.4.6. Discard the **methylene chloride** phase.

11.1.4.7. Add 6 mL of cold (4°C) 1:1 sulfuric acid to the sample. Seal, and shake to mix. Check the pH of the sample with pH paper. If the pH is not ≤ 2, and more acid to adjust the pH to ≤ 2.

Caution: Addition of acid may cause heat and / or pressure build up.

11.1.4.8. Add 100 mL diethyl ether to the sample and extract by shaking or rotating vigorously for 10 minutes, venting as necessary. Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

11.1.4.9. Drain the aqueous layer into a clean flask or beaker. Collect the ether phase in a clean flask or bottle containing approximately 10g of acidified anhydrous sodium sulfate.

11.1.4.10. Return the aqueous phase to the separatory funnel, add 100 mL diethyl ether and repeat the extraction procedure a second time, combining the ether extracts. Repeat the extraction a third time with 100 mL diethyl ether. Discard the aqueous phase after the third extraction.

11.1.4.11. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken.

11.1.4.12. Proceed to Section 11.5, Concentration.

11.2. Extraction of soil and sediment samples

11.2.1. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

11.2.2. Weigh 50.0 g of moist solid sample into a clean glass jar. Use 50 g of sodium sulfate for the Method Blank and the LCS. Acidify the sample with 5 mL of concentrated HCl.

11.2.3. There should be a small amount of liquid phase. If not, add reagent water until there is. Stir well with a spatula. (Note: This is not necessary for the method blank or LCS)

11.2.4. After 15 minutes, stir with a spatula and check the pH of the liquid phase. Add more acid if necessary to bring the pH to <2, repeating the stirring and standing time after each acid addition. (Note: The pH of the method blank and LCS are not determined.)

11.2.5. Add 60 g of acidified sodium sulfate and mix well. The sample should be free flowing. If not, add more sodium sulfate.

11.2.6. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2)

11.2.7. Add a minimum of 100 mL of 1:1 methylene chloride:acetone to the beaker or 100 mL of methylene chloride for long list (dinoseb).

11.2.8. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.2.9. Sonicate for 3 minutes, making sure the entire sample is agitated.

11.2.10. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.2.11. Place the prepared funnel on a collection apparatus. If the herbicide esters are *not* to be determined, the collection apparatus is a bottle or flask containing approximately 10g of anhydrous acidified sodium sulfate. If the

herbicide esters *are* to be determined, (normally the case) the collection apparatus is glassware suitable for the hydrolysis step, typically a KD flask or Turbovap tube.

11.2.12. Decant and filter extracts through the prepared funnel into the collection apparatus.

11.2.13. Repeat the extraction two more times with additional 100 mL minimum portions of the appropriate solvent each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone.

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.2.14. If the herbicide esters are not to be determined, dry the extract as described in Section 11.4 or go to cleanup, Section 11.3. If the herbicide esters are to be determined (normally the case) proceed to Section 28.2.15

11.2.15. Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Check the pH with pH paper. If the pH is not $\geq$12, adjust with additional KOH.

11.2.16. Heat on a water bath at 60-65°C for 2 hours. Allow to cool. Higher temperatures, up to 90°C, may be used if needed to remove the ether layer within 2 hours.

11.2.17. Transfer the solution to a separatory funnel and extract three times with 100 mL portions of methylene chloride. **Discard the methylene chloride phase.** The aqueous solution contains the herbicides.

11.2.18. Adjust the pH of the solution to $\leq$2 with 1:1 sulfuric acid.

11.2.19. Extract three times with 60 mL diethyl ether.

11.2.20. Proceed to Section 11.3, Cleanup, if required, or Section 11.4, Extract drying.

11.3. Cleanup

11.3.1. This cleanup step may be necessary if the procedure for determining the herbicide acids only is being followed. (See Section 28.2.14) It is not normally required if the acids and esters

are being determined. (The usual case.) If cleanup is not required, proceed to Section 28.4, Extract drying.

11.3.2. Prepare 45 mL of basic extraction fluid by mixing 30 mL of reagent water with 15 mL of 37% KOH. Use three 15 mL portions of this fluid to partition the extract from section 28.2.12 or 28.2.20, using a small separatory funnel. **Discard the organic phase.**

11.3.3. Adjust the pH of the solution to ≤2 with cold (4°C) sulfuric acid. (1:1). Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

Caution: Addition of acid may cause heat and / or pressure build up.

11.4. Extract drying

11.4.1. Pour the extracts through a funnel containing acidified sodium sulfate into a flask or bottle containing approximately 10 g acidified sodium sulfate. Rinse the funnel with a little extra diethyl ether.

11.4.2. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken. Proceed to Section 28.5, concentration.

11.5. Concentration

11.5.1. Transfer the ether extract into a Turbovap concentrator tube or a 500 mL K-D flask **equipped with a 10 mL concentrator tube. Use** a stirring rod to crush the caked sodium sulfate during transfer. Rinse the flask or bottle with 20-30 mL ether to complete transfer.

11.5.2. Attach a three ball Snyder column to the K-D apparatus, prewet the column with a few mL of ether from the top, and place the apparatus on a water bath at approximately 60°C. At the proper rate of distillation, the balls of the column will chatter, but the chambers will not flood. When the apparent volume reaches 2 mL, remove from the water bath and allow to completely cool.

11.5.3. For TCLP extracts only, add 4 mL of toluene to the K-D (buffer reacts with diazald solution used in esterification).

11.5.4. Remove TCLP extracts at approximately 2 mL when boiling slows and only toluene is remaining. Cool and cap in CT.

11.5.5. Carefully disassemble the concentrator tube and rinse the lower glass joint with a small amount of diethyl ether.

11.5.6. The extract is now ready for esterification by the Diazomethane Bubbler Method (Section 11.7) or the TCLP esterification by Boron Triflouride Method (Section 11.8).

11.6. Esterification (Bubbler Method)

11.6.1. Assemble the diazomethane apparatus (see figure below) in a hood. Add 25-30 mL of diethyl ether to tube 1. Add 1.5 mL 37% KOH, 1 mL Carbitol, and 1 mL of ether and 3-4 g of diazald to tube 2.

11.6.2. Place the tip of the disposable pipette into the vial containing the first sample extract. Apply nitrogen flow (approx. 10 mL/min) to bubble diazomethane through the sample extract for about 4-5 minutes. Replace the disposable pipette and place the tip into the vial containing the second extract. Replace Tube 2 solution after second extract.

11.6.3. Allow the extracts to stand for 20 minutes, then add approximately 0.2 g of silica gel to each extract. Allow to stand for an additional 20 minutes.

11.6.4. Adjust the volume to 10 mL with hexane. The sample is now ready for gas chromatography.

11.6.5. A routine 10X dilution occurs on final extracts for all samples. Due to a QuantIMS limitation, the dilution factor field in QuantIMS cannot be used when a dilution is routine, because the dilution factor is automatically applied to all reference values creating reporting problems. For the herbicide analysis, the extract volume will be 10mL and an aliquot at 10X dilution will be analyzed. The final extract volume recorded on the laboratory bench sheet will be recorded as 100mL to avoid using the dilution factor field in QuantIMS.

11.7. Esterification by Boron trifluoride (TCLP extracts only).

11.7.1. To the concentrator tube with the extract, add 2 mL of Boron trifluoride. Place a two-ball micro-Snyder column on the concentrator tube and place in the Hot-Blok water bath adjusted to 35-40°C for 60 minutes. Remove and let cool for approximately ten minutes.

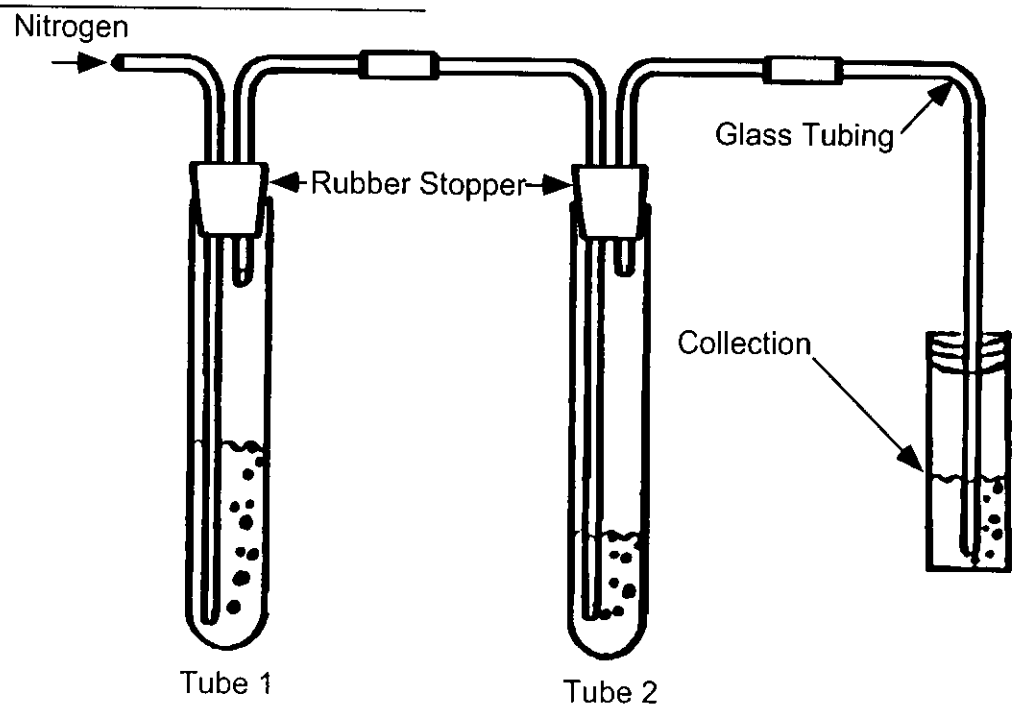
11.7.2. With a 10 mL graduated disposable 5-3/4" pipette 4.5 mL of 5% neutral sodium sulfate and place it in the concentrator tube. Seal with a tight fitting ground glass stopper. Vortex the mixture for one minute. Let stand for ten minutes to settle. With a 5-3/4" disposable pipette, withdraw the bottom aqueous layer into a 16 x 100 culture tube for proper disposal.

11.7.3. Prepare a clean up column in a 5-3/4" disposable pipette by placing a small amount of glass wool in the narrow end of the pipette and add about ½ inch – 1 inch of florisil and sodium sulfate each. Leave about a 1 inch gap at the top. Place the extract in the clean-up column and gently force it through by using a pipette bulb into a small test tube. **Care should be taken to avoid channeling.** Rinse the concentrator tube with 1-2 mL of toluene. Transfer the column rinsate into the test tube. Rinse the column with additional toluene. There should be approximately 4 mL collected in the test tube. Bring the final volume to 10 mL with toluene by visually comparing it to a calibrated collection tube.

Note: It is critical that all toluene is retained and no water should enter the column.

11.8 Esterification by Trimethylsilydiazomethane

11.8.2 Exchange the extract into Hexane and concentrate to 2.0 mls. 200 uL of Methanol is added to the extract then 100 uL of the trimethylsilyldiazomethane solution. The extract then turns a yellow colour. If this does not occur, then an additional 100 uL aliquot is added until the yellow persists. The extract then sits for 1 hour at room temperature to allow the methylation reaction to proceed. After 1 hour, the reaction is halted and the diazomethane removed by the addition of silicic acid. The extract is then brought up to a final volume of 10.0 mls with Hexane and submitted for analysis.



12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Refer to CORP-GC-0001 for details of method performance.

14. POLLUTION PREVENTION

14.1. Refer to Section 14 of the main body of this SOP.

15. WASTE MANAGEMENT

15.1. Refer to Section 15 of the main body of this SOP.

15.2. The following waste streams are produced when this method is carried out.

15.2.1. **Aqueous acidic waste.** These wastes are disposed of in the liquid-liquid separation unit

15.2.2. **Non-hazardous sodium sulfate**. Non hazardous substances can be disposed of in the regular trash.

16. REFERENCES

16.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Chlorinated Herbicides, Method 8151A.

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Directions to add sufficient reagent water to the soil sample so that the pH can be measured have been added (Section 11.5.2)

17.1.2. The bubbler esterification method uses methanolic KOH in place of the aqueous KOH / carbitol mixture recommended in method 8150B. This has been found to provide a more effective and reliable esterification.

17.2. Modifications from previous revisions

17.2.1. References have been updated

17.3. Tables

Table A1
Herbicide Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
Herbicides	Herbicides Water	1.0
Herbicides	Herbicides Soil	1.0

Table A2
Herbicide Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
Herbicides	Herbicides MS-Soil	1.0
Herbicides	Herbicides MS-Water	1.0

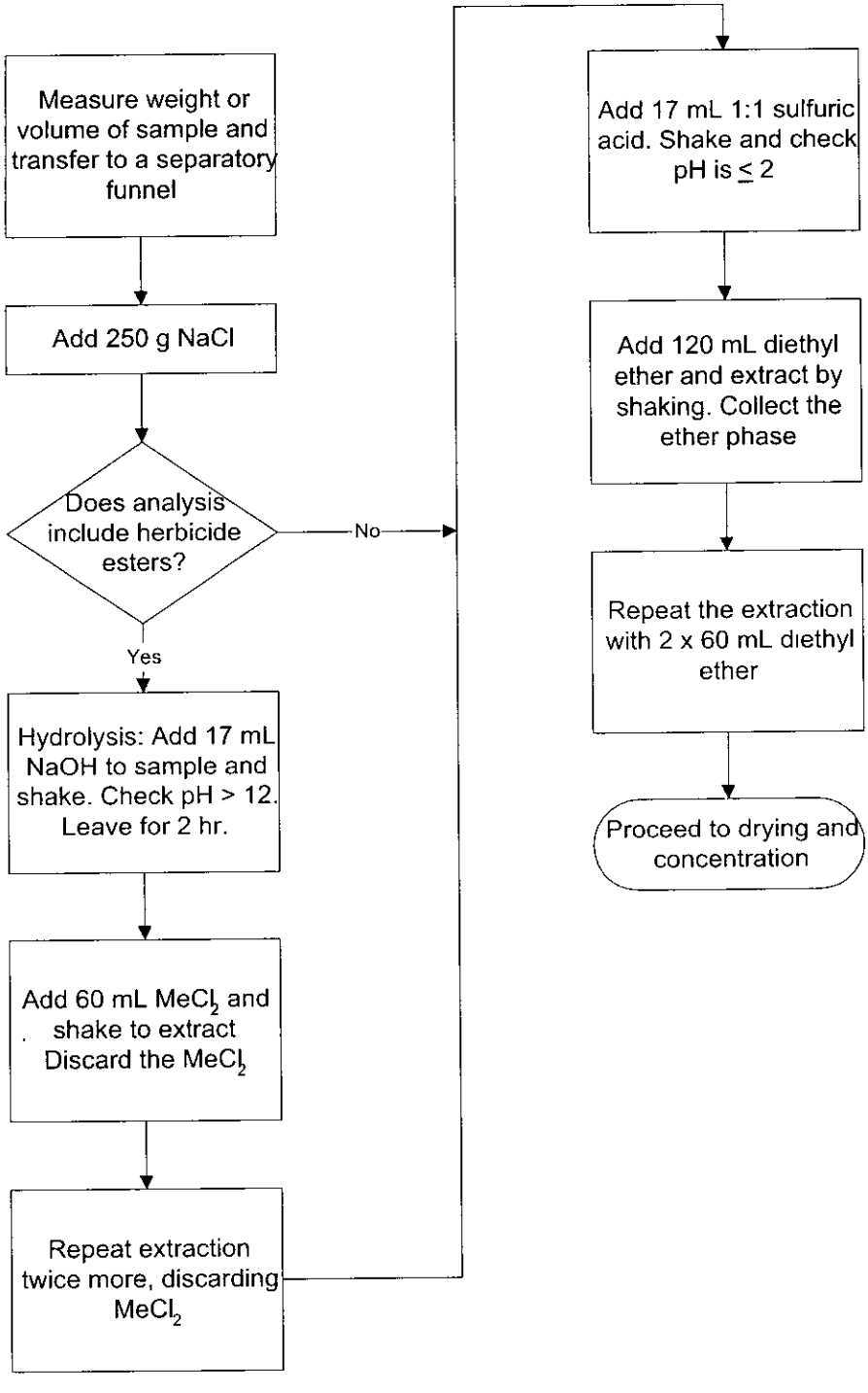
Table A3 Herbicide Surrogate Spike Components			
Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides WS	2,4-DCAA	Acetone	2
Herbicides SS	2,4-DCAA	Acetone Methanol	20

[1]The surrogate is spiked as the free acid

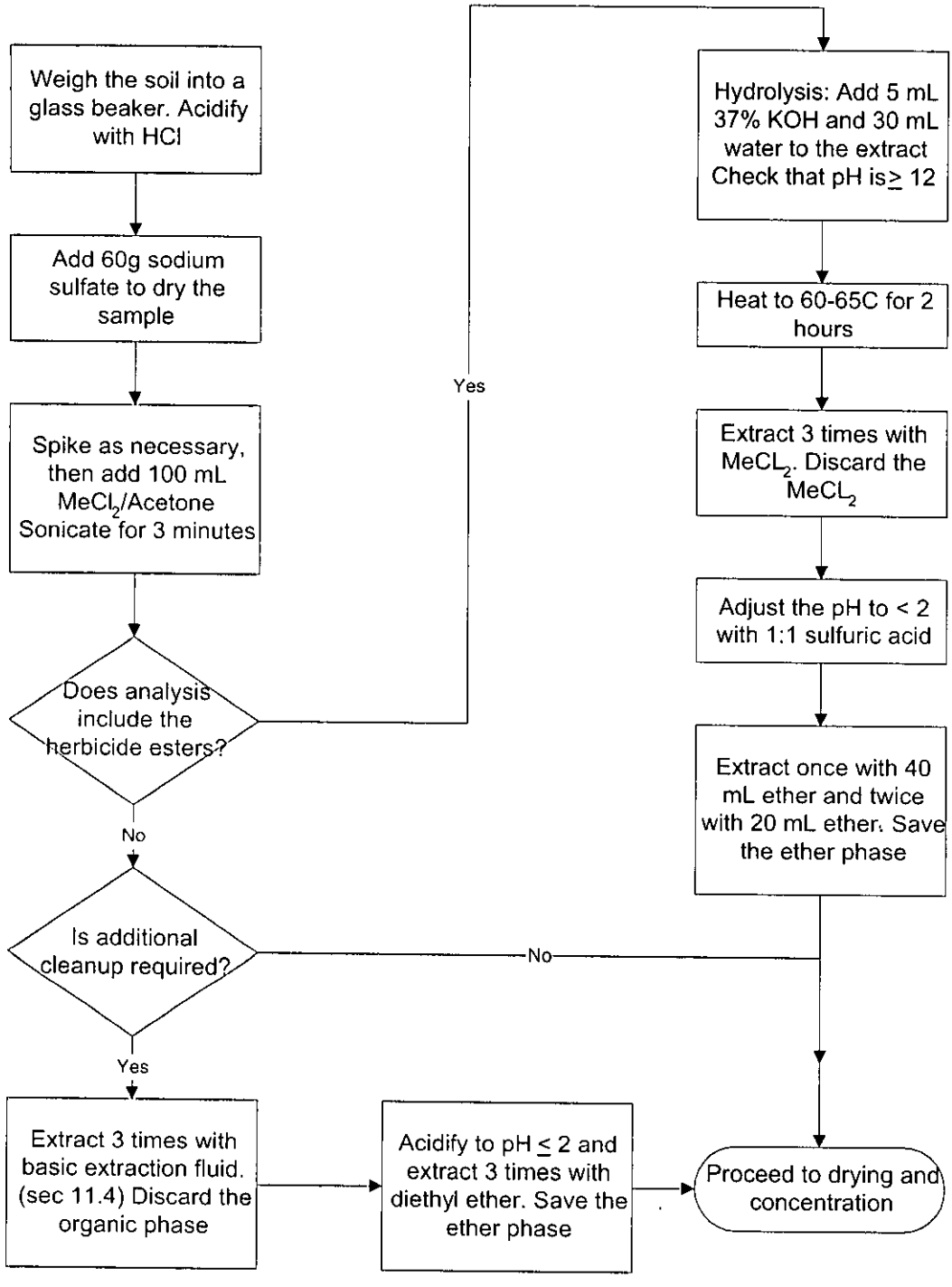
Table A4 Herbicide Matrix Spike Components				
Type	Compounds[1]	Compounds[1] Solvent	Water/Soil Conc. (ug/mL)	TCLP only Conc. (ug/mL)
Herbicides MS	2,4-D	Methanol	16	2
	2,4-DB		16	2
	2,4,5-TP (Silvex)		4	0.5
	Dalapon		8	1
	Dicamba		8	1
	Dichloroprop		16	1
	Dinoseb		2.5	0.3
	2,4,5-T		4	0.5
	MCPA		1600	
	MCPP		1600	
	Pentachlorophenol		2	

[1]The herbicide spiking solution contains the herbicides as the free acids.

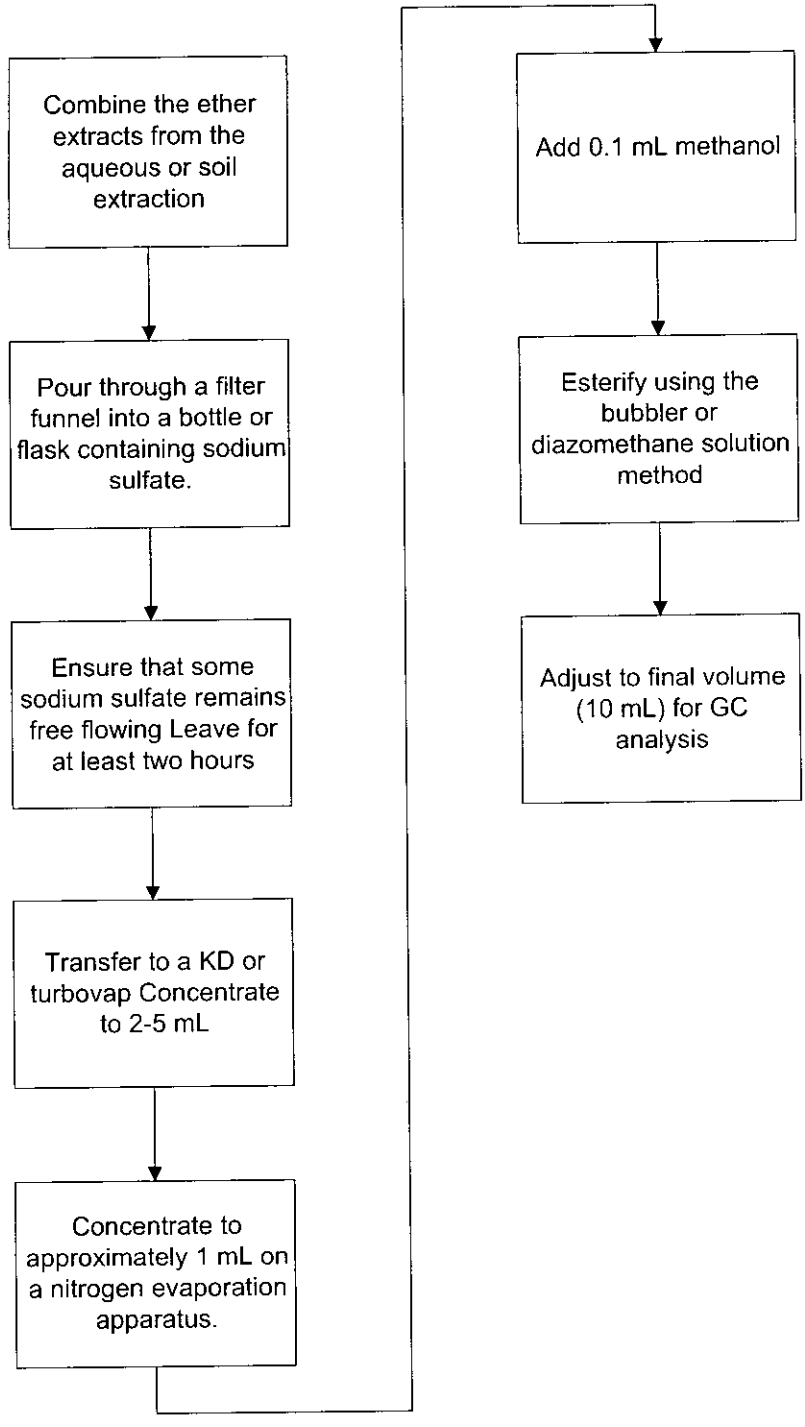
Extraction of Aqueous Samples



Extraction of Soils and Sediments



Drying, Concentration and Esterification



STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, SW846 7470A AND MCAWW 245.1

(SUPERSEDES: REVISION 2.4, DATED 10/28/02)

Prepared by:		1/21/04 Date
Approved by:	Technical Specialist	1.21.04 Date
Approved by:	Quality Assurance Manager	1/21/04 Date
Approved by:	Environmental, Health and Safety Coordinator	1/21/04 Date
Approved by:	Laboratory Director	1/29/04 Date

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TABLE OF CONTENTS

LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A and MCAWW Method 245.1.

1.2. The associated LIMs method codes are BL (Method 245.1) and O8 (Method 7470A).

1.3. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.4. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, TCLP, and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed, however Method 7471A (see CORP-MT-0007NC) is usually the method of choice. All matrices require sample preparation prior to analysis.

1.5. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters and domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.6. The STL North Canton reporting limit for mercury in aqueous matrices is 0.0002 mg/L except for TCLP or SPLP leachates for which the reporting limit is 0.002 mg/L.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate, which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility.

4.5. Samples containing high concentrations of oxidizing organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low.

4.6. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be

	Poison		fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent
Mercury (1,000 ppm in Reagent)	Oxidizer Corrosive Poison	0 1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain May cause dermatitis, burns, and moderate skin necrosis

1 – Always add acid to water to prevent violent reactions.

2 – Exposure limit refers to the OSHA regulatory exposure limit.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

5.6. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.7. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders are located outside the laboratory and the gas led to the instrument through approved lines.

5.8. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath capable of maintaining a temperature of 90-95 °C.

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump, which can deliver 1 L/min, air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that achieve the same purpose are also acceptable (i.e., Gortex filter).

6.3. 8oz. HDPE Plastic bottles.

6.4. Nitrogen or argon gas supply, welding grade, or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Thermometer (capable of accurate readings at 95 °C).

6.8. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (10 ppm) mercury standards (in 10% HNO_3) are purchased as custom STL North Canton solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working mercury standard (0.1 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. The calibration standards listed in Table I must be prepared fresh daily from the working standard (7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water.

7.5. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.6. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.7. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.8. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9. Stannous chloride solution: Add 50 g of stannous chloride and 25 mL of concentrated hydrochloric acid to a 500mL volumetric flask and bring to volume with deionized water.

7.10. Sodium chloride-hydroxylamine hydrochloride solution: Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to every 2000 mL of reagent water.

7.11. Potassium permanganate, 5% solution (w/v): Dissolve 100 g of potassium permanganate for every 2000 mL of reagent water.

7.12. Potassium persulfate, 5% solution (w/v): Dissolve 100 g of potassium persulfate for every 2000 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7470A or the 245.1, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL North Canton reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A batch is a group of no greater than 20 samples excuding QC Samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples witin the batch must be treated with the same lots of reagents and the same processes. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit or at or above 10% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level).

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).
- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**
- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative.**

9.4. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the

method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the instance where the LCS recovery is > 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be addressed in the project narrative.
- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.
- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results, which fall outside the control limits, must be addressed in the narrative.
- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not

necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.6. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.8 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the ICV, ICB, CRA, CCV, and CCB with the calibration curve.

9.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.8 for required run sequence.) The CCB result must fall within +/- RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

9.8. Detection Limit Standard (CRA)-To verify linearity at the reporting limit, a CRA standard is run at the beginning of each sample analysis run after the ICV/ICB. The CRA standard mercury concentration is 0.2 ug/L. Recovery must be ± 50% of the true value, or the standard is either rerun or the problem corrected and the instrument recalibrated. (See Section 11.2.8 for the required run seuquence.)

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences, which cause a baseline shift. Refer to Section 11.2.9 for additional information on when full 4 point MSA is required as well as Appendix B for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer and listed in Appendix F. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL North Canton reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥ 0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (7.3) into a series of 100 ml class A volumetrics, then dilute to volume . For the ICV, use a 2.5 ml aliquot of the working standard. The ICV working standard must be made from a source other than that used for the calibration standards.

11.1.2. Transfer 100 mL of well-mixed sample or standard to a clean sample digestion bottle.

Note: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

Note: Spiking is done before the addition of acids or reagents.

11.1.3. Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 mixing after each addition.

11.1.4. Add 15 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 25-mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

Note: When performing analyses using automated vs. manual techniques the sample dilution resultant from the addition of more than the original aliquot of permanganate solution must be compensated for by the addition of the same volume of permanganate to all other associated samples and standards in the run. In instances, where this is not feasible, the addition of excess reagent can be addressed through mathematical correction of the results to account for the resultant dilution effect.

11.1.5. Add 8 mL of potassium persulfate solution and heat for two hours in a water bath at 90 - 95 °C.

11.1.6. Cool samples.

11.2. Sample Analysis:

11.2.1. Refer to the Appendix F of this SOP for detailed setup and operation protocols.

11.2.2. When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains). Add this solution in 6-mL increments until the permanganate is completely reduced.

11.2.3. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.4. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.5. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.6. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.7. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.8. The following run sequence is consistent with 7470A, CLP and 245.1.

Instrument Calibration
ICV
ICB
CRA
CCV
CCB
10 samples

CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for Quality Control criteria to apply to Methods 7470A and 245.1.

11.2.9. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and matrix spike levels for TCLP analyses are detailed in Table I (Appendix A). Appendix B provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data are reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMs after final technical review.

11.6. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.7. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%\,R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = \text{C x D}$$

Where:

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.6. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.7. Appropriate factors must be applied to sample values if dilutions are performed.

12.8. Sample results should be reported with up to three significant figures in accordance with the STL North Canton significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Method performance is determined by the analysis of method blanks, laboratory control samples, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.3. The laboratory control sample should recover within 20% of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

15.3. Waste Streams Produced by the Method

15.3.1. **Acid Waste- Aqueous waste generated by the analysis.** Samples are disposed of in the acid waste drum located in the metals lab. The contents of the drum are neutralized and released to the POTW.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

16.1.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.1.

16.1.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0 and ILMO4.0.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. STL Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003.

16.2.2. Glassware Washing, NC-QA-0014.

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021.

16.2.5. Navy/Army SOP, NC-QA-0016.

16.2.6. Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, Method 245.1 CLP-M, SOW ILM03.0 and SOW ILM04.0 SOP, CORP-MT-0006NC, current version.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7470A and 245.1.

17.1.1.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

17.1.2. Modifications from Method 7470A

17.1.2.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the

method blank must not contain any analyte of interest at or above the reporting limit.

17.1.3. Modifications from 245.1

17.1.3.1. Method 245.1 Section 9.3 states concentrations should be reported as follows: Between 1 and 10 ug/L, one decimal; above 10 ug/L, to the nearest whole number. STL North Canton reports all Hg results under this SOP to two significant figures.

Figure 1. Aqueous Sample Preparation - Mercury

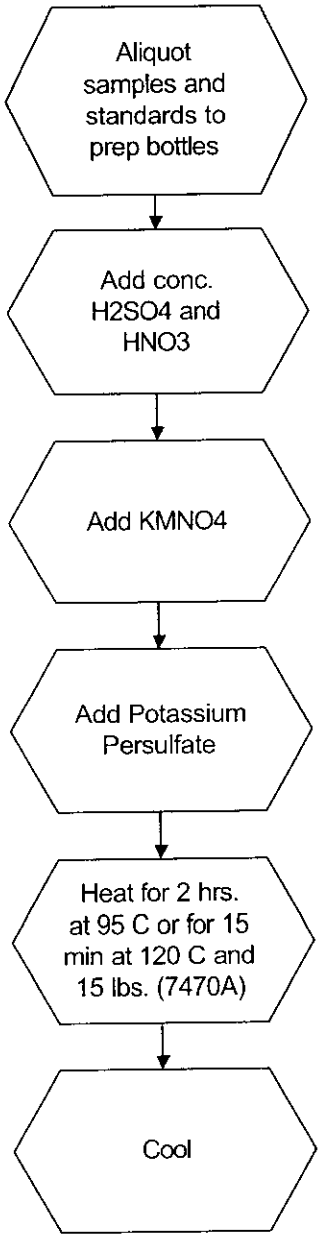

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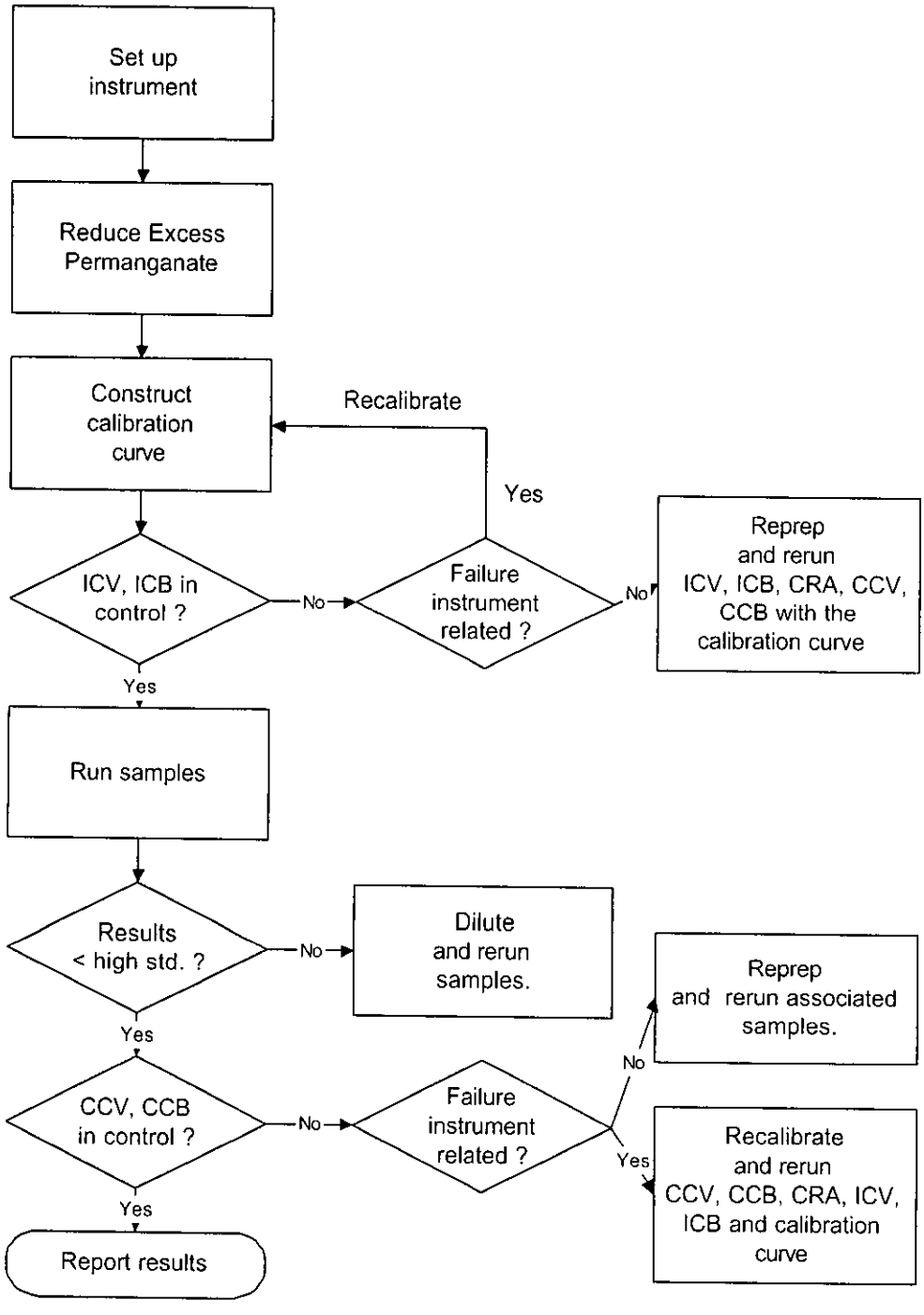
Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (MG/L)

Standard Aqueous RL	0.0002
TCLP RL	0.002
Std 0	0
Std 1/CRA	0.0002
Std 2	0.0005
Std 3	0.001
Std 4	0.005
Std 5	0.010
ICV	0.0025
LCS/CCV	0.005
Aqueous MS	0.001
TCLP MS	0.005

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	90-110 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve. (See Section 9.6).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve. (See Section 9.6).
CRA	Beginning of every analytical run following theICB and prior to sample analyses.	50-150% recovery	Rerun to verify; or correct problem and recalibrate or reprep with the calibration curve (See Sec. 9.8)
CCV	Every 10 samples and at the end of the run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve. (See Section 9.7).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep with calibration curve. (See Section 9.7).

Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.3).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.3 for additional requirements.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.4).
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.5) For TCLP see Section 11.2.9
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%. (See MS)	See Corrective Action for Matrix Spike.

APPENDIX B

MSA GUIDANCE

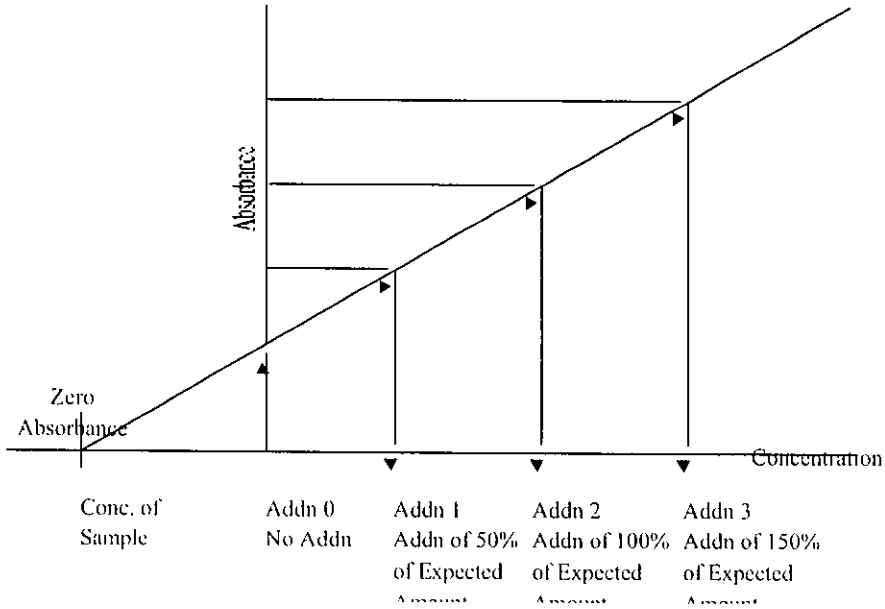
APPENDIX B. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX C

TROUBLESHOOTING GUIDE

APPENDIX C. TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on "Continuous"
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won't Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX D

CONTAMINATION CONTROL GUIDELINES

APPENDIX D. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Alternatively, vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX E

PREVENTIVE MAINTENANCE

APPENDIX E. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200II)

Daily	As Needed
Check nitrogen flow.	Check Hg lamp intensity.
Check tubing.	Clean lens.
Check drain.	Check aperture.
	Replace drying tube
	Change Hg lamp.
	Check liquid/gas separator.

APPENDIX F

INSTRUMENT SET UP

Hg Analysis (Leeman PS200II)

SYSTEM INITIALIZATION AND WARM UP

1. F1 Menu

2. Instrument

a. TASKMASTER

b. #4 Wake System Up Enter

The warming up period takes approximately 10 minutes.

TO SET UP INSTRUMENT FOR ANALYSIS

1. F1 Menu

2. Autosampler

A. Rack Entry

B. Edit (ex. Rack 1), Enter

C. Cup ID - Enter (clears sample #'s)

D. Extended ID- type in matrix of sample (water or solid), Enter.

E. Press Insert Key and move cursor with arrows to cup ID and begin typing labels.

F. F3 Print Screen

3. Press F2 Macro key and type in analyst's first name - Enter

A. Enter folder name - ex. HG0306, Enter. If folder does not exist, type Y - Enter.

B. Type in - "Rack 1", "Rack 2" etc. , Enter.

C. Type in : FROM CUP TO CUP

Ex. = 1 30

Do the same for position 2 if needed. If not needed, you must press Enter 3 times to begin analysis.

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Implementation Date: 12/3/02

SOP No. CORP-MT-0007NC
Revision No. 2.4
Revision Date: 10/28/02
Page 1 of 43

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY, SW846 7471A AND MCAWW 245.5
(SUPERSEDES: REVISION 2.3, DATED 05/15/01)

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Corporate Technology

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TABLE OF CONTENTS

LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7471A and MCAWW Method 245.5.

1.2. The associated LIMs method code is O9.

1.3. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.4. Methods 7471A and 245.5 are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits, wastes, wipes and sludge-type materials. All matrices require sample preparation prior to analysis.

1.5. The STL North Canton reporting limit for mercury in solid matrices is 0.033 mg/kg based on a 0.6 g sample aliquot (wet weight).

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in hydrochloric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

5.6. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.7. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.8. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining temperature of 90- 95 °C).

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump which can deliver 1 L/min air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that acheive the same purpose are also acceptable (i.e., Gortex filter).

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Top-loading balance, capable of reading up to two decimal places.

6.8. Thermometer (capable of accurate readings at 95 °C).

6.9. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (10 ppm) mercury standards (in 10% HNO_3) are purchased as custom STL North Canton solutions. All standards must be stored in FEP fluorocarbon or previously unused

polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working mercury standard (0.1 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. The calibration standards must be prepared fresh daily from the working standard (7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample preparation bottles and proceeding as specified in Section 11.1

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.5. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.6. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.7. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.8. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.10. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.11. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

Note: Stannous chloride may be used in place of stannous sulfate. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.12. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.13. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of sample analysis.

8.2. Soil samples do not require preservation but must be stored at 4° C ± 2° C until the time of analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7471A or the 245.5, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL North Canton reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to

monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level).

- Reprepparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the

method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 70-130% recovery must be applied.

- In the instance where the LCS recovery is > 130% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative."

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 70 - 130 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not

necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% of the true value for that solution . An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.10 and Section 11.2.11 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include reprepparation of the ICV, ICB, CRA, CCV and CCB with the calibration curve.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.10 and 11.2.11 for required run sequence.) The CCB result must fall within +/- RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.2.12 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL North Canton reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Standard and Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples.

11.1.2. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (7.3) into a series of sample digestion bottles. For the ICV, transfer a 2.5 ml aliquot of the working standard. The ICV working standard must be made from a source other than that used for the calibration standards.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

11.1.3. Add reagent water to each standard bottle to make a total volume of 10 mL. Continue preparation as described under 11.1.5 below.

11.1.4. Transfer triplicate 0.2 g portions of a well mixed sample into a clean sample digestion bottle. Add 10mL of reagent water to each standard bottle. Continue

preparation as described under 11.1.5.

11.1.5. Water Bath protocol:

11.1.5.1. To each **standard** bottle: Add 5 mL of aqua regia.
To each **sample** bottle: Add *10* mL of reagent water and 5 mL of aqua regia.

11.1.5.2. Heat for 2 minutes in a water bath at 90 - 95 ° C.

11.1.5.3. Add *40* mL of distilled water.

11.1.5.4. Add 15 mL of potassium permanganate solution.

11.1.5.5. Heat for 30 minutes in the water bath at 90 - 95 °C.

11.1.5.6. Cool.

11.1.5.7. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.

11.1.5.8. To each **standard** bottle: Add 50 mL of reagent water.
To each **sample** bottle: Add *50* mL of reagent water.

11.1.5.9. Continue as described under Section 11.2.

11.2. Sample Analysis:

11.2.1. Because of differences between various makes and models of CVAA instrumentation, no detailed operating instructions can be provided. Refer to the facility specific instrument operating SOP and the CVAA instrument manual for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. Manual determination:

11.2.3.1. Treating each sample individually, purge the head space of the sample bottle for at least one minute.

11.2.3.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.3.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.3.4. Place the aeration device into 100 mLs of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.4. Automated determination: Refer to Appendix G for instrument setup and operation.

11.2.5. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. ug of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.6. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.7. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.8. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.9. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.10. The following analytical sequence must be used with 7471A and 245.5:

Instrument Calibration
ICV
ICB

Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7471A and 245.5.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.11. The following run sequence is consistent with 7471A, CLP and 245.5 and may be used as an alternate to the sequence in 11.2.10. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
CRA*
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOP (CORP-MT-0008) for quality control requirements for QC samples.

* Refer to the CLP SOP for information on the CRA.

11.2.12. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.6. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%\ R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result
DU2 = Sample duplicate result

12.5. For automated determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

$$mg/kg,\ dry\ weight = (C \times V \times D)/(W \times S)$$

Where:

C = Concentration (ug/L) from instrument readout
V = Volume of digestate (L)
D = Instrument dilution factor
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.6. For manual (total) determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

$$mg/kg,\ dry\ weight = \quad (C)/(W \times S)$$

Where:

C = Concentration (ug) from instrument readout
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Sample results should be reported with up to three significant figures in accordance with the STL North Canton significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.1.

13.2. Method performance is determined by the analysis of method blank, laboratory control sample, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 30 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.4. The laboratory control sample should recover within 20% of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury).

16.1.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.5.

16.1.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0 and IMLO4.0.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.2. STL Laboratory Quality Manual (LQM), current version. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7471A and 245.5.

17.1.1.1. A potassium persulfate oxidation step has been included to facilitate the breakdown of organic mercurials which are not completely oxidized by potassium permanganate. Use of potassium persulfate in combination with the permanganate improves the recovery of mercury from organo-mercury compounds. The use of persulfate has been incorporated in several recent EPA mercury protocols.

17.1.1.2. The alternate run sequence presented in Section 11.2.11 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7471A

17.1.2.1. Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.2.2. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.3. Modifications from 245.5

17.1.3.1. Method 245.5 Section 9.3 states concentrations should be reported as follows: Between 0.1 and 1 ug/g, to the nearest 0.01 ug; between 1 and 10 ug/g, to the nearest 0.1ug; above 10 ug/g, to the nearest ug. STL North Canton reports all Hg results under this SOP to two significant figures.

17.2. Modifications from previous SOP

17.2.1. Section 1.4 reporting limit changed form 0.1 mg/kg based on a 0.2 g to 0.3 mg/kg based on a 0.6 g sample aliquot

17.2.2. Section 9.3 added MS and MSDs as not counted in determination of preparation batches.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.

Non-conformance summary (if applicable).

Figure 1. Solid Sample Preparation for Mercury - Water Bath Procedure

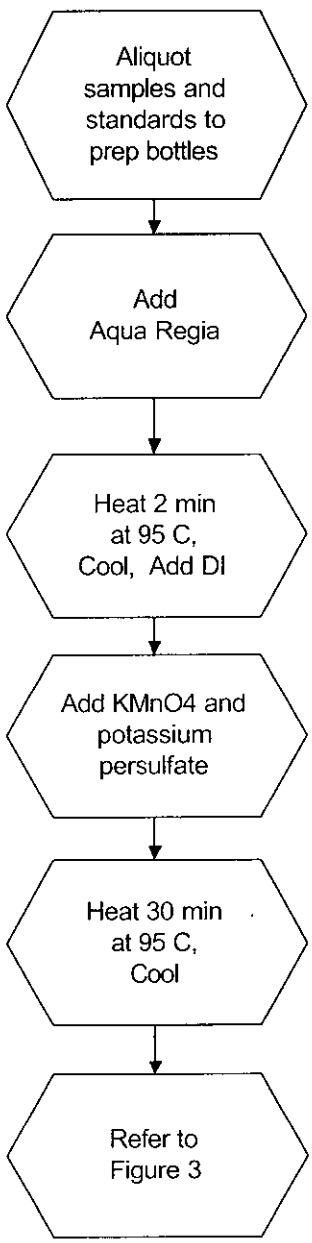
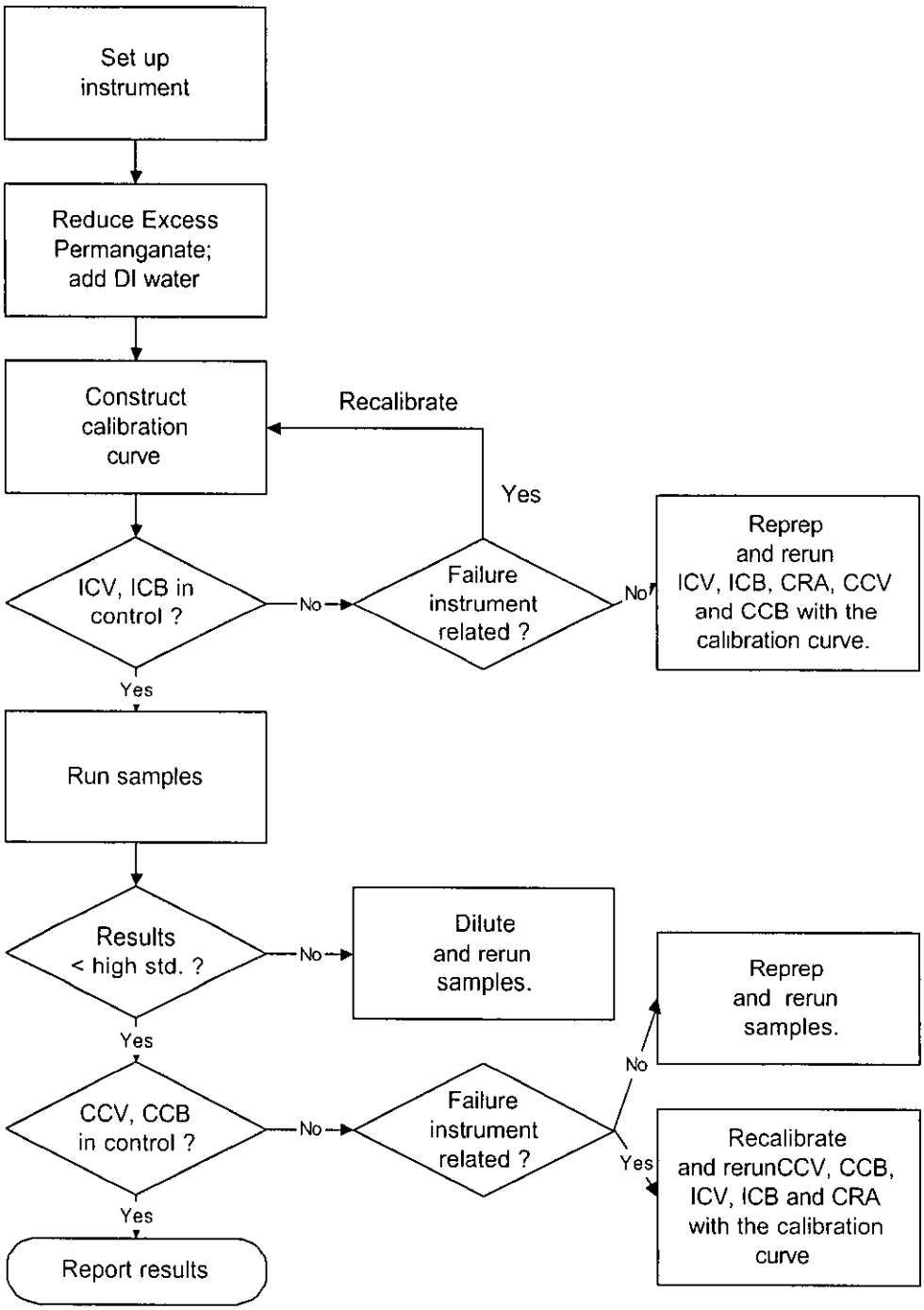


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS

Soil RL (mg/kg)	0.1
Std 0 (mg/L)	0
Std 1 (mg/L)	0.0002
Std 2 (mg/L)	0.0005
Std 3 (mg/L)	0.001
Std 4 (mg/L)	0.005
Std 5 (mg/L) **	0.010
ICV (mg/L)	0.001 or 0.0025 ***
CCV/LCS (mg/L)	0.0025 or 0.005 ***
MS (mg/L)	0.001

* **SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.**

** **Optional standard which may be used to extend the calibration range as allowed by the instrument configuration. If the instrument configuration prevents the use of 6 standards, the 2 ppb standard may be eliminated in favor of the 10 ppb standard.**

*** **Concentration level dependent on high calibration standard used. CCV must be 50% of the high standard concentration and the ICV must be 20-25% of the high standard concentration.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	90-110 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve (see Section 9.7).
CCV	Every 10 samples and at the end of the run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep with calibration curve (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4)	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.

*See Sections 11.2.10 and 11.2.11 for exact run sequence to be followed.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 11.3.12
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%. (See MS)	See Corrective Action for Matrix Spike.

APPENDIX B

EXAMPLE
STL NORTH CANTON Hg DATA REVIEW CHECKLIST

Example
STL North Canton Hg Data Review Checklist

Run/Project Information

Run Date: _____ **Analyst:** _____ **Instrument:** _____
Prep Batches Run: _____

Circle Methods used: **7470A / 245.1 :** CORP-MT-0005 Rev 1 **7471 / 245.5** : CORP-MT-0007 Rev 1
CLP - AQ : CORP-MT-0006 Rev 0 **CLP - SOL** : CORP-MT-0008 Rev 0

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2ndLevel
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?				
4. CRA run (CLP only)?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/MDL data on file?				
3. Calculations and Transcriptions checked for error ?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct ?				

Analyst: _____ **Date:** _____
Comments:

_____
_____
_____

2nd Level Reviewer : _____ **Date:** _____

_____
_____
_____

APPENDIX C

MSA GUIDANCE

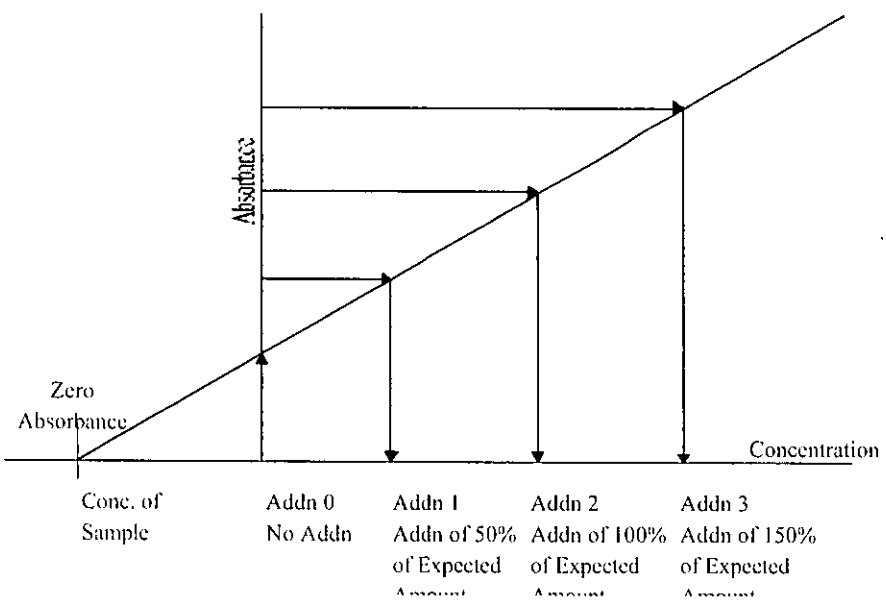
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D. TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on "Continuous"
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won't Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200) [1]

Daily	Semi-annually	Annually
Clean lens.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture.		Check liquid/gas separator.
Check argon flow.		
Check tubing.		
Check drain.		
Replace drying tube.		

Cold Vapor Atomic Absorption (PE 5000) [1]

Daily	Monthly
Clean aspirator by flushing with DI water.	Clean cell in aqua regia.
Check tubing and replace if needed.	Clean aspirator in aqua regia.
Clean windows with methanol.	
Change silica gel in drying tube.	
Check argon gas supply.	
Adjust lamp.	

APPENDIX G

INSTRUMENT SET UP

Hg Analysis (Leeman PS200II)

SYSTEM INITIALIZATION AND WARM UP

1. F1 Menu
2. Instrument

a. Taskmaster

b. #4 Wake System Up Enter

The warming up period takes approximately 10 minutes.

TO SET UP INSTRUMENT FOR ANALYSIS

1. F1 Menu
2. Autosampler
    A. Rack Entry
    B. Edit (ex. Rack 1), Enter
    C. Cup ID - Enter (clears sample #'s)
    D. Extended ID- type in matrix of sample (water or solid), Enter.
    E. Press Insert Key and move cursor with arrows to cup ID and begin typing labels.
    F. F3 Print Screen
3. Press F2 Macro key and type in analyst's first name - Enter
    A. Enter folder name - ex. HG0306, Enter. If folder does not exist, type Y - Enter.
    B. Type in - "Rack 1", "Rack 2" etc. , Enter.

D. Type in : FROM CUP TO CUP

Ex. = 1 30

Do the same for position 2 if needed. If not needed, you must press Enter 3 times to begin analysis.

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Implementation Date: 1/22/04

SOP No. CORP-MT-0001NC
Revision No. 3.4
Revision Date: 01/08/04
Page 1 of 54

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSES, SW-846 METHOD 6010B AND EPA METHOD 200.7

(SUPERSEDES: REVISION 3.3, REVISION DATE (12/05/01)

Approved by: _____ 1/12/04
Date

Approved by: _____ 1-12-2004
Technical Specialist Date

Approved by: _____ 1-21-04
Quality Assurance Manager Date

Approved by: _____ 1-19-2004
Environmental, Health and Safety Coordinator Date

Approved by: _____ 1/20/04
Laboratory Manager Date

Approved by: _____ 1/22/04
Technical Director Date

Proprietary Information Statement:

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TABLE OF CONTENTS

LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) using SW-846 Method 6010B and EPA Method 200.7 . Table I of Appendix A lists the elements appropriate for analysis by Methods 6010B and 200.7. Additional elements may be analyzed under Methods 6010B and 200.7 provided that the method performance criteria presented in Section 13.0 are met.

1.2. ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the matrices and instrumentation used.

1.3. Method 6010B is applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, biological, and TCLP, EP and other leachates/extracts. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators may require digestion of **dissolved samples** and this must be clarified and documented before project initiation. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples if the criteria in Section 11.1 are met. Silver concentrations must be below 0.1 mg/L in aqueous samples.

1.5. State-specific requirements may take precedence over this SOP for drinking water sample analyses.

1.6. The applicable LIMS method codes are QO (6010B), QM (6010B Trace), AS (200.7), JI (200.7 Trace). The Trivalent Chromium method code is GU.

2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line

emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed.

2.2. Refer to CORP-IP-0002NC, Acid Digestion of Soils, SW846 Method 3050B and CORP-IP-0003NC, Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods for details on sample preparation methods.

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following vigorous digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.

- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.1.1. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.1.2. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.1.3. Physical interferences are generally considered to be effects associated with sample transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard and/or use of a high solids nebulizer can reduce the effect.

4.1.4. Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching or standard addition procedures.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves

that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4-ppm STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3.1. The plasma emits strong UV light and is harmful to vision. **NOTE: AVOID looking directly at the plasma**.

5.3.2. The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Metals digestates can be processed outside of a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.2. Radio Frequency Generator.

6.3. Argon gas supply, welding grade or equivalent.

6.4. Coolflow or appropriate water cooling device.

6.5. Peristaltic Pump.

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.7. Class A volumetric flasks.

6.8. Autosampler tubes.

7. REAGENTS AND STANDARDS

7.1. Intermediate standards are purchased as custom STL North Canton multi-element mixes or as single-element solutions. All standards must be stored in FEP fluorocarbon or unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided,

the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the acceptance criteria described in laboratory-specific SOPs are met.

7.2. Working calibration and calibration verification solutions may be used for up to 3 months and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in a matrix of 5% hydrochloric and 5% nitric acids. Refer to Tables III, IV, IVA, V and VI (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, interference correction and spiking solutions.

7.3. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.4. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.5. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding times for metals are six months from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Soil samples do not require preservation but must be stored at 4°C ± 2° until the time of preparation .

9. QUALITY CONTROL

Table VII (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

9.1.1. Prior to analysis of any analyte using either Method 200.7 or Method 6010B, the following requirements must be met.

9.1.2. Instrument Detection Limit (IDL) - The IDL for each analyte must be determined for each analyte wavelength used for each instrument. The IDL must be determined

annually. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined. The IDL shall be determined by multiplying by 3, the standard deviation obtained from the analysis of a blank solution, with seven consecutive measurements. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure performed between the analysis of separate samples). The result of the IDL determination must be below the STL North Canton reporting limit. The CLP IDL procedure can be used for this method.

9.1.3. Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any client samples. Refer to STL North Canton SOP NC-QA-0021 for details on MDL analysis and criteria.

9.1.4. Linear Range Verification (LR) - The linear range must be verified every 6 months on at least an annual basis for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample. The standards used to verify the linear range limit must be analyzed during a routine analytical run and must read within 5% of the expected value.

For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across the estimated range. One standard should be near the upper limit of the estimated range. The concentration measured at the LDR must be no more than 10% less than the expected level extrapolated from lower standards. If the instrument is adjusted in any way that may affect the LRs, new dynamic ranges must be determined. The LR data must be documented and kept on file.

9.1.5. Background Correction Points - To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the ICP instrument manual for specific procedures to be used in setting background correction points.

9.1.6. Inter-element Corrections (IECs) - ICP interelement correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be redetermined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables (e.g. MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to

evaluate the validity of the IECs. Refer to the instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than ± the RL as defined in Tables I, IA or II. For elements with a reporting limit 10 ug/L or less, the signal should be ± 2X the RL. To determine IECs, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the actual concentration of the "interfering element."

Note: Trace ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the Trace as reflected by the ICSA response. Additional spectral interference is present from easily ionizable elements such as potassium and sodium in axial viewing instruments.

9.1.7. Rinse Time Determination - Rinse times must be determined upon initial set-up of an ICP instrument. To determine the appropriate rinse time for a particular ICP system, the linear range verification standard (see 9.1.4) should be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system. For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

9.2. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20x higher than the blank contamination level).

- If the analyte is a common laboratory contaminant (copper, iron, lead (Trace only) or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. Such action must be addressed in the project narrative.

- Reprepparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be addressed in the project narrative.

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative.

- For dissolved metals samples which have not been digested, a CCB result is reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.3. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table III (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

- If any analyte is outside established control limits the system is out of control and corrective action must occur. Unless in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the event that an MS/MSD analysis is not possible a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- In the instance where the LCS recovery is greater than 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be addressed in the report narrative.

- Corrective action will be reprepparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

- For dissolved metals samples which have not been digested, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Tables III and VI (Appendix A).

- If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. For both methods 200.7 and 6010B, control limits of 75-125% recovery and 20% RPD or historical acceptance criteria must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data are reported as NC, MSB (i.e., not calculated). Two other narrative notes for metals analyses: Matrix spike/spike duplicate spike recovery/recoveries was/were outside the acceptance limits of some analytes. The acceptable LCS analysis data indicated that the analytical system was operating within control and this condition is most likely due to matrix interference. See the Matrix Spike Report for the affected analytes which will be flagged with N. Matrix spike/spike duplicate relative percent difference (RPD) exceeded the acceptance limits for some analytes. The imprecision may be attributed to sample heterogeneity. See the Matrix Spike Report for the affected analytes, which will be flagged with *.

- If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- For dissolved metals samples which have not been digested, a MS/MSD must be performed per batch of up to 20 samples by spiking two aliquots of the sample at the levels specified in Table III (Appendix A).

9.5. Dilution test – A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix. One sample per preparation batch must be processed as a dilution test. The test is performed by running a sample at a 5x (1:4) dilution. Samples identified as field blanks cannot be used for dilution tests. The results of the diluted sample, after correction for dilution, should agree within 10% of the original sample determination when the original sample concentration is greater than 50x the IDL. If the results are not within 10%, the possibility of chemical or physical interference exists and the data is flagged.

9.6. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). For analyses conducted under Method 200.7, the ICV result must fall within 5% of the true value for that solution with relative standard deviation <3% from replicate (minimum of two) exposures. For Method 6010B, the ICV must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the RL from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the calibration reverified. (See Section 11.8 or 11.11 for required run sequence).

9.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the sample run. The CCV is be a mid-range standard made from a dilution of the calibration standard. The CCV for both methods must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. A CCB is analyzed immediately following each CCV. (See Section 11.8 or 11.11 for required run sequence.) The CCB result must fall within +/- RL from zero. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, reanalysis and recalibration are not required before continuation of the run. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, all affected samples will be re-analyzed with valid CCV/CCB pairs. (Refer to Section 11.13 for an illustration of the appropriate rerun sequence).

9.8. Interference Check Analysis (ICSA/ICSAB) - The validity of the interelement correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Table V (Appendix A) for the details of ICSA and ICSAB composition. Custom

STL North Canton multielement ICS solutions must be used. All analytes should be spiked into the ICSAB solution, therefore, if a non-routine analyte is required then it should be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix. If the ICP will display overcorrection as a negative number then the non-routine elements can be controlled from the ICSA as described in section 9.8.3. Elements known to be interferents on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium and magnesium must always be included in all ICP runs.

9.8.1. The ICSA and ICSAB solutions must be run at the beginning of the run. (See Section 11.10 or 11.13 for required run sequence.)

9.8.2. The ICSAB results for the interferents must fall within 80 - 120% of the true value. If any ICSAB interferent result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the samples rerun.

9.8.3. ICSA results for the non-interfering elements with reporting limits ≤ 10 ug/L must fall within the STL North Canton guidelines of ± 2x RL from zero. ICSA results for the non-interfering elements with RLs> 10 µg/L must fall within the STL North Canton guidelines of ± 1x RL from zero. If the ICSA results for the non-interfering elements do not fall within +/- 2x RL (RL ≤10) or ± 1xRL (RL>10) from zero the field sample data must be evaluated as follows:

- If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.
- If the affected element was not required then the sample data can be accepted.
- If the interfering elements are not present in the field sample at a concentration which would result in a false positive or negative result greater than +/- 2x RL from zero then the field sample data can be accepted.
- If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than ± 2x RL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.
- If the data does not meet the above conditions then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to the

raw results. If the results are recalculated manually the calculations must be clearly documented on the raw data.

9.9. CRI - To verify linearity near the RL for ICP analysis, a CRI standard is run at the beginning of each sample analysis run. Additionally, some projects may require CRI analysis at the end of the run. (See Section 11.10 or 11.13 for required run sequence.) Evaluate associated samples based upon advisory limits of +/- 50% of true value.

Note: The custom STL North Canton CRI mix contains most analytes at a level near the standard lab reporting limit.

Note: For certified Ohio drinking water analysis, the CRI concentration must be at or below the reporting limit and must recover at ± 30% of true value.

9.10. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.17 for additional information on when MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the instructions in Appendix G.

10.2. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures. Flush the system with the calibration blank between each standard or as the manufacturer recommends. The calibration curve must consist of a minimum of a blank and a standard. Refer to Appendix G for detailed set up and operation protocols.

10.3. Calibration must be performed daily and each time the instrument is set up. Instrument runs may be continued over periods exceeding 24 hours as long as all calibration verification (CCV) and interference check QC criteria are met. The instrument standardization date and time must be included in the raw data.

10.4. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corresponding corrective actions.

11. PROCEDURE

11.1. For 200.7 analyses, dissolved (preserved) samples must be digested unless it can be documented that the sample meets all of the following criteria:

A. Visibly transparent with a turbidity measurement of 1 NTU or less.

B. Is of one liquid phase and free of particulate or suspended matter following acidification.

C. Is NOT being analyzed for silver.

11.2. A minimum of two exposures for each standard, field sample and QC sample is required. The average of the exposures is reported. For Trace ICP analyses, the results of the sum channel must be used for reporting.

11.3. Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 9.1.5 it can be demonstrated that a shorter rinse time may be used.

11.4. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV,CCV), blanks (ICB,CCB,PB), interference checks (ICSA,ICSAB) and field samples (linear range) to improve the data review process.

11.5. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.6. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run.

11.7. The use of an internal standard is **required** on the Trace ICP unless the calibration and QC standards are matrix matched to each digestion procedure used as follows:

Preparation Method	% HNO_3	% HCl
CLP Aqueous	1	5
CLP Soil	5	2.5
SW846 3050	10	10
SW846 3005	2	5

SW846 3010	6	5

The following procedural guidelines must be followed when using an internal standard:

11.7.1. Typically used internal standards are: yttrium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

11.7.2. The internal standard (IS) must be added to every sample and standard at the same concentration. It is recommended that the IS be added to each analytical sample automatically through use of a third pump channel and mixing coil. Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

11.7.3. The concentration of the internal standard should be sufficiently high to obtain good precision in the measurement of the IS analyte used for data correction and to minimize the possibility of correction errors if the IS analyte is naturally present in the sample.

11.7.4. The internal standard raw intensity counts must be printed on the raw data.

11.7.5. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte). The instrument automatically adjusts sample results based on comparison of the internal standard intensity in the sample to the internal standard intensity at calibration.

11.7.5.1. If the internal standard counts fall within ±30% of the counts observed in the ICB then the data is acceptable.

11.7.5.2. If the internal standard counts in the field samples are more than ±30% higher than the expected level, the field samples must then be diluted and reanalyzed.

11.8. The following analytical sequence must be used for Methods 6010B and 200.7:

Instrument Calibration
ICV
ICB
CRI

ICSA
ICSAB
7 samples
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of up to 10 samples between CCV/CCB pairs as required to complete run
CRI (The CRI counts as a sample analysis.)
CCV
CCB

Refer to Quality Control Section 9.0 and Table VII (Appendix A) for Method 6010B and 200.7 quality control criteria.

11.9. Additional quality control analyses are necessary for analysis under the Contract Laboratory Program (CLP). If these are included then CLP, 6010 and 200.7 samples can be included in the same sequence. Refer to CORP-MT-0002NC for details.

11.10. Full method required QC must be available for each wavelength used in determining reported analyte results.

11.11. The following run sequence provides an illustration of a mid-run CCV or CCB failure and the appropriate corrective action run sequence as described in Section 9.7:

Original Run: Instrument Calibration

ICV

ICB

CRI

ICSA

ICSAB

7 samples

CCV1

CCB1

10 samples

CCV2

CCB2

10 samples **

CCV3 * * Failure occurs at CCV3/CCB3

CCB3 * **Samples requiring rerun for affected analytes

10 samples **

CCV4

CCB4

10 samples

CCV5

CCB5

Reanalysis: Recalibrate

ICV

ICB

CRI

ICSA

ICSAB

CCV2

CCB2

10 samples

CCV3

CCB3

10 samples

CCV4

CCB4

Notes: Samples between CCV4 and CCV5 do not require reanalysis as they were bracketed by compliant QC samples.

See CORP-MT-0002NC for the appropriate reanalysis sequence if CLP requirements must also be met.

11.14 The instrument may be reprofiled between CCV/CCB pairs to correct for environment induced drift.

11.15 Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.16 All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. If an interelement correction exists for an analyte which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an overrange analyte may not be required to be reported for a sample, if that analyte is a interferent for any requested analyte in that sample, the sample must be diluted. Acid strength must be maintained in the dilution of samples.

11.17 For TCLP samples, full four-point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and regulatory limits for TCLP analyses as well as matrix spike levels are detailed in Table VI (Appendix A). Appendix C provides guidance on performing MSA analyses.

11.18 Any variation in procedure shall be completely documented using instrument run logs, maintenance logs, report narratives, a Nonconformance Memo, or an anomaly report and

is approved by a Supervisor/Group Leader and QA Manager. If contractually required, the client shall be notified by the Project Manager.

11.19 Nonconformance documentation shall be filed in the project file.

11.20 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.21 Analytical Documentation

11.21.1 Record all analytical information in the analytical logbook/logsheet which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.21.2 All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.21.3 Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.21.4 Sample results and associated QC are entered into the LIMs after final technical review.

12 DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

12.5. The final concentration for a digested aqueous sample is calculated as follows:

$$mg / L = \frac{C \times V1 \times D}{V2}$$

Where:

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6. The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$mg / Kg, dry\ weight = \frac{C \times V \times D}{W \times S}$$

Where:

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:

I = Sample result (Instrument reading)

S = Dilution test result (Instrument reading × 5)

12.9. Appropriate factors must be applied to sample values if dilutions are performed.

12.10. Sample results should be reported with up to three significant figures in accordance with the STL North Canton significant figure policy.

12.11. Trivalent Chromium

12.11.1. Trivalent chromium (CR^{+3}) is the result obtained by subtracting the hexavalent chromium (CR^{+6}) results for a sample from the total chromium result from that sample. The total chromium result is determined using the procedures in this SOP. The hexavalent chromium result is determined using the procedures in STL North Canton SOP NC-WC-0024.

12.11.2. Reporting Limits

12.11.2.1. The STL North Canton water reporting limit for trivalent chromium is 0.02 mg/l.

12.11.2.2. The STL North Canton solid reporting limit for trivalent chromium is 2.0 mg/kg, wet weight.

12.11.3. Calculations: Cr^{+3} = Cr, total – Cr^{+6}

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Refer to Tables I, IA & II in Appendix A for the list of Method 6010B and 200.7 analytes as well as additional analytes that may be analyzed using this SOP.

13.3. Method performance is determined by the analysis of MS and MSD samples as well as method blanks and laboratory control samples. The MS or MSD recovery should fall within +/- 25 % and the MS/MSD should compare within 20% RPD or within the laboratory's historical acceptance limits. These criteria apply to analyte concentrations greater than or equal to 10xIDL. Method blanks must meet the criteria specified in Section 9.2. The laboratory control samples should recover within 20% of the true value or within the laboratory's historical acceptance limits.

13.4. Training Qualification:

13.4.1. The group/team leader or the supervisor has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.2. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15.2. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.3. Waste Streams Produced by this Method

15.3.1 The following waste streams are produced when this method is carried out:

15.3.2 Acid waste consisting of sample and rinse solution - Any sample waste generated must be collected and disposed of in the acid waste drum located in the metals lab.

15.3.3 Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1. References

16.1.1. 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits.

16.1.2. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996. Method 6010B.

16.1.3. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7.

16.1.4. Inductively Coupled Plasma – Atomic Emission Spectrometric Method for Trace Element Analysis of water and wastes Method 200.7, 40 CFR – Chapter I – Part 136 – Appendix C. Electronic version dated September 30, 2002.

16.1.5. CORP-MT-0002NC, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Method 200.7 & CLP-M, SOW ILMO3.0 and ILMO4.0).

16.1.6. Corporate Quality Management Plan (QMP), current version

16.1.7. STL Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA-003, STL North Canton QC Program.

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

16.2.6. QA-004, Rounding and Significant Figures.

16.2.7. NC-WC-0024, Hexavalent Chromium (Colorimetric)

16.2.8. CORP-IP-0002NC, Acid Digestion of Soils, SW846 Method 3050B

16.2.9. CORP-IP-0003NC, Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method

17.1.1. Modifications/interpretations from both Methods 6010B and 200.7.

17.1.1.1. STL North Canton laboratories use mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.

17.1.1.2. Methods 200.7 and 6010B state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. In determining IECs, because of lack of definition clarification for "concentration range around the calibration blank," STL North Canton has adopted the procedure in EPA CLP ILMO4.0.

17.1.1.3. Section 8.5 of Method 6010B and Section 9.5 of Method 200.7 recommend that whenever a new or unusual matrix is encountered, a series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because STL North Canton laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, STL North Canton may select to perform a dilution test on one sample in each prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At STL North Canton, matrix interference is determined by evaluating data for the LCS and MS/MSD. STL North Canton REQUIRES documented, clear guidance when a new or unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

17.1.2. Modifications from Method 200.7.

17.1.2.1. Method 200.7 defines the IDL as the concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength. STL North Canton labs utilize the IDL definition as defined in Section 9.1 of this SOP.

17.1.2.2. The calibration blank is prepared in an acid matrix of 5% HNO_3/5% HCl instead of the specified 2% HNO_3/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.

17.1.2.3. Method section 9.3.4 specifies that "Analysis of the IPC (ICSA/AB) solution immediately following calibration must verify that the instrument is within ± 5% of calibration with a relative standard deviation <3% from replicate integrations ≥ 4." STL North Canton uses a minimum of two exposures.

17.1.2.4. The 40 CFR version of Method 200.7 requires the instrument check standard to agree within ± 5% of expected values. Also, the 40 CFR version requires the interference check sample to be analyzed at the beginning, end, and at periodic intervals throughout the sample run. At STL North Canton, the instrument check standard equals the CCV, which must agree within ± 10% of expected values, and the ICSA standards are analyzed only at the beginning of a sample run. STL's procedures are in line with the Rev. 4.4, May 1994 version of Method 200.7.

17.1.2.5. Section 7.12 of 200.7 indicates that the QCS (ICV) should be prepared at a concentration near 1 ppm. The ICV specified in this SOP accommodates the 1 ppm criteria for the majority of analytes. For the remaining analytes, this SOP specifies ICV concentrations which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.

17.1.2.6. The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 section 10.4 states that results should fall within the established control limits of 3 times the standard deviation of the

calibration blank for that analyte. The control limits listed in this SOP are those applicable to the EPA designed solution.

17.1.2.7. Method 200.7 section 9.3.4 states the CCB should be less than the IDL, but > the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL North Canton has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. SOP section 9.7 provides the detailed corrective action criteria that must be followed.

17.1.3. Modifications from Method 6010B.

17.1.3.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.3.2. Method 6010B section 8.6.1.3 states that the results of the calibration blank are to agree within 3x the IDL. If not, repeat the analysis two or more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL North Canton has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. See SOP Section 9.7 for a detailed description of the required corrective action procedures.

APPENDIX A

TABLES

TABLE I. Method 200.7 and 6010B Target Analyte List

ELEMENT	Symbol	CAS #	6010B analyte	200.7 analyte	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	X	200	20
Antimony	Sb	7440-36-0	X	X	60	6
Arsenic	As	7440-38-2	X	X	300	30
Barium	Ba	7440-39-3	X	X	200	20
Beryllium	Be	7440-41-7	X	X	5.0	0.5
Boron	B	7440-42-8	X	X	200	20
Cadmium	Cd	7440-43-9	X	X	5.0	0.5
Calcium	Ca	7440-70-2	X	X	5000	500
Chromium	Cr	7440-47-3	X	X	10	1
Cobalt	Co	7440-48-4	X	X	50	5
Copper	Cu	7440-50-8	X	X	25	2.5
Iron	Fe	7439-89-6	X	X	100	10
Lead	Pb	7439-92-1	X	X	100	10
Magnesium	Mg	7439-95-4	X	X	5000	500
Manganese	Mn	7439-96-5	X	X	15	1.5
Molybdenum	Mo	7439-98-7	X	X	40	4
Nickel	Ni	7440-02-0	X	X	40	4
Potassium	K	7440-09-7	X	X	5000	500
Selenium	Se	7782-49-2	X	X	250	25
Silver	Ag	7440-22-4	X	X	10	1
Sodium	Na	7440-23-5	X	X	5000	500
Thallium	Tl	7440-28-0	X	X	2000	200
Vanadium	V	7440-62-2	X	X	50	5
Zinc	Zn	7440-66-6	X	X	20	2

TABLE IA. Method 200.7 and 6010B Trace ICP Target Analyte List

ELEMENT	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Arsenic	As	7440-38-2	10	1.0
Lead	Pb	7439-92-1	3.0	0.3
Selenium	Se	7782-49-2	5.0	0.5
Thallium	Tl	7440-28-0	10	1.0
Antimony	Sb	7440-36-0	10	1.0
Cadmium	Cd	7440-43-9	2.0	0.2
Silver	Ag	7440-22-4	5.0	0.5
Chromium	Cr	7440-47-3	5.0	0.5

TABLE II. Non-Routine Analyte List

ELEMENT	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Tin	Sn	7440-31-5	100	10
Titanium	Ti	7440-32-6	50	5

TABLE III. Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	LCS Level (ug/L)	Matrix Spike Level (ug/L)
Aluminum	2000	2000
Antimony	500	500
Arsenic	2000	2000
Barium	2000	2000
Beryllium	50	50
Cadmium	50	50
Calcium	50000	50000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1000	1000
Lead	500	500
Magnesium	50000	50000
Manganese	500	500
Molybdenum	1000	1000
Nickel	500	500
Potassium	50000	50000
Selenium	2000	2000
Silver	50	50
Sodium	50000	50000
Thallium	2000	2000
Vanadium	500	500
Zinc	500	500
Boron	1000	1000
Tin	2000	2000
Titanium	1000	1000

TABLE IV. ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	100000	200	25000	50000
Antimony	10000	60	1000	5000
Arsenic	10000	300	1000	5000
Barium	10000	200	1000	5000
Beryllium	10000	5	1000	5000
Cadmium	10000	5	1000	5000
Calcium	100000	5000	25000	50000
Chromium	10000	10	1000	5000
Cobalt	10000	50	1000	5000
Copper	10000	25	1000	5000
Iron	100000	100	25000	50000
Lead	10000	100	1000	5000
Magnesium	100000	5000	25000	50000
Manganese	10000	15	1000	5000
Molybdenum	10000	40	1000	5000
Nickel	10000	40	1000	5000
Potassium	100000	5000	25000	50000
Selenium	10000	250	1000	5000
Silver	2000	10	500	1000
Sodium	100000	5000	25000	50000
Thallium	20000	2000	5000	10000
Vanadium	10000	50	1000	5000
Zinc	10000	20	1000	5000
Boron	10000	200	1000	5000
Tin	10000	100	1000	5000
Titanium	10000	50	1000	5000

TABLE IVA. Trace ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	50000	200	12500	25000
Antimony	1000	10	250	500
Arsenic	1000	10	250	500
Barium	4000	10	1000	2000
Beryllium	4000	5	1000	2000
Cadmium	1000	2	250	500
Calcium	100000	5000	25000	50000
Chromium	4000	5	1000	2000
Cobalt	4000	50	1000	2000
Copper	4000	25	1000	2000
Iron	50000	100	12500	25000
Lead	1000	3	250	500
Magnesium	100000	5000	25000	50000
Manganese	4000	15	1000	2000
Molybdenum	4000	40	1000	2000
Nickel	4000	40	1000	2000
Potassium	100000	5000	25000	50000
Selenium	1000	5	250	500
Silver	2000	5	500	1000
Sodium	100000	5000	25000	50000
Thallium	2000	10	500	1000
Vanadium	4000	50	1000	2000
Zinc	4000	20	1000	2000

TABLE V. Interference Check Sample Concentrations*

Element	ICSA (ug/L)	ICSAB (ug/L)
Aluminum	500000	500000
Antimony	-	1000
Arsenic	-	1000
Barium	-	500
Beryllium	-	500
Cadmium	-	1000
Calcium	500000	500000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200000	200000
Lead	-	1000
Magnesium	500000	500000
Manganese	-	500
Molybdenum	-	1000
Nickel	-	1000
Potassium	-	10000
Selenium	-	1000
Silver	-	1000
Sodium	-	10000
Thallium	-	10000**
Vanadium	-	500
Zinc	-	1000
Tin	-	1000
Boron		1000
Titanium		1000

* Custom STL North Canton solutions contain analytes common to all STL North Canton facilities. Non-routine elements not listed above should be spiked into the ICSAB at 1000 ug/L.

** Thallium level for Trace ICP should be at 1000 ug/L.

TABLE VI. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	Reporting Level (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

TABLE VII. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Two-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met		Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	Method 200.7: 95 - 105 % recovery. RSD dupl. exp < 3% Method 6010B: 90 - 110 % recovery. RSD dupl. exp < 5%	Terminate analysis; Correct the problem; Recalibrate.
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate.
CCV	Every 10 samples and at the end of the run.	Method 200.7 & 6010B: 90 - 110 % recovery. RSD dupl. exp < 5%	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.
CRI	Beginning of every run	50-150% recovery (advisory)	Evaluate associated samples.
ICSA	Beginning of every run	See Section 9.8.3	See Section 9.8.3
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.8.2.

* See Sections 11.10 and 11.13 for exact run sequence to be followed.

TABLE VII. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Dilution Test	One per prep batch.	For samples > 50x IDL, dilutions must agree within 10%.	Narrate the possibility of physical or chemical interference per client request.
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Common lab contaminants may be accepted up to 2x the RL (See 9.2). Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require redigestion or reanalysis (see Section 9.2).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.2 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits. Samples for which the contaminant is < RL and the LCS results are > 120% may not require redigestion or reanalysis (see Section 9.3)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.

TABLE VII. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. For TCLP See Section 11.17.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. For TCLP see Section 11.17.
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery; RPD ≤ 20% .	See Corrective Action for Matrix Spike.

APPENDIX B

CROSS REFERENCE OF TERMS USED IN METHODS 6010B, 200.7, AND BY STL NORTH CANTON

CROSS REFERENCE OF TERMS COMMONLY USED IN METHODS EPA 200.7, SW6010B, AND STL NORTH CANTON INC. SOP

EPA 200.7	SW6010B	STL North Canton Inc. SOP
Calibration blank (CB)	Calibration blank	Initial and continuing calibration blanks (ICB/CCB)
Dilution test	Dilution test	Dilution Test
Instrument detection limit (IDL)	Instrument detection limit (IDL)	Instrument detection limit (IDL)
Instrument performance check (IPC)	Continuing calibration verification (CCV)	Continuing calibration verification (CCV)
Internal standard	Internal standard	Internal standard (IS)
Laboratory duplicates	n/a	n/a
Laboratory fortified blank (LFB)	n/a	Laboratory control sample (LCS)
Laboratory fortified sample matrix (LFM)	Matrix spike and matrix spike duplicate (MS/MSD)	Matrix spike and matrix spike duplicate (MS/MSD)
Laboratory reagent blank (LRB)	Method blank	Method or Prep blank (MB)
Linear dynamic range (LDR)	Linear dynamic range (LDR)	Linear dynamic range (LDR)
Method detection limit (MDL)	Method detection limit (MDL)	Method detection limit (MDL)
Quality control sample (QCS)	Check standard or Initial calibration verification (ICV)	Initial calibration verification (ICV)
Spectral interference check solution (SIC)	Interference check solution (ICS)	Interference check solution (ICSA/ICSAB)

APPENDIX C

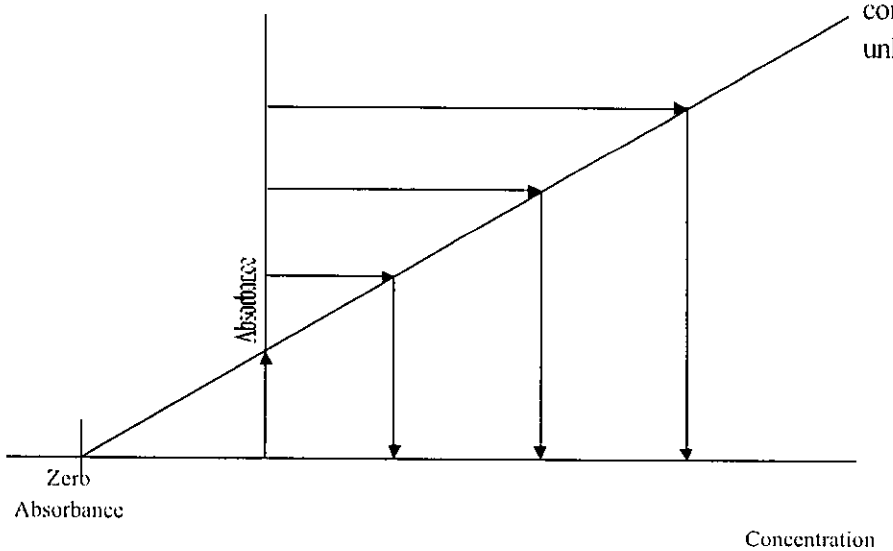
MSA GUIDANCE

Appendix C. MSA Guidance

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown.



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.

- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D. TROUBLESHOOTING GUIDE

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer Clean or replace mixing chamber Lower Torch
Instrument Drift	RF not cooling properly Vacuum level is too low Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Reprofile Horizontal Mirror Replace PA tube
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Cu/Mn Ratio Outside Limits or Low Sensitivity	Plasma conditions changed Clean nebulizer, torch or spray chamber Replace tubing (clogged) Realign torch Check IECs
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipet tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Daily	Change sample pump tubing and pump windings Check argon gas supply level Check rinse solution and fill if needed Check waste containers and empty if needed Check sample capillary tubing is clean and in good condition Check droplet size to verify nebulizer is not clogged. Check sample flow for cross flow nebulizer Check Cu/Mn ratio-should be 30% of value at date that IECs were performed Check pressure for vacuum systems
As Needed	Clean plasma torch assembly to remove accumulated deposits Clean nebulizer and drain chamber; keep free-flowing to maintain optimum performance Replace peristaltic pump tubing, sample capillary tubing and autosampler sipper probe
Weekly	Apply silicon spray on autosampler tracks Check water level in coolflow
Monthly	Clean air filters on back of power unit to remove dust Check D mirror for air instruments
Bi-yearly	Change oil for vacuum systems Replace coolant water filter (may require more or less frequently depending on quality of cooling water)

APPENDIX G

ICP OPERATING INSTRUCTIONS

ICP Analysis (TJA 61E)

(Example)

1. SETUP

a. Plasma Control Panel (enter)

b. (F1)-Startup

c. (F9)-Continue

d. (F2)-Levels

1. Change auxiliary gas to low – use space bar to toggle
2. Change nebulizer gas flow to 0.5 L/min.
3. Change pump rate to 130
4. Esc
5. Allow instrument to warm up approximately 30 minutes.

2. DEVELOPMENT

a. Methods (enter)

b. Enter method name

c. (F3)-Method Info.

d. Change file name

e. (F9)-Done

f. (F9)-Done/Keep

18. OPERATION

a. Analysis (enter)

b. (F5)-Profile

1. (F3)-Automatic

2. (F1)-Run

3. If peak position is greater than +/- .05 units from the center peak position, you must adjust the profile. If it is within +/- .05 units, press (F9)-done.

4. To adjust select (F1)-CalcSS and enter current vernier position. (enter)

5. Adjust to new vernier position(F9)-done

6. Rerun profile until peak position is +/- .05 units.

7. (F9)-Done

c. Autosampler (F9)

1. Enter method name (enter)

2. Enter autosampler table name (enter)

3. (F1)-Run

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Implementation Date: 4/25/03

SOP No. CORP-IP-0002NC
Revision No. 2.4
Revision Date: 02/19/03
Page 1 of 26

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF SOILS, SW846 METHOD 3050B

(SUPERSEDES: REVISION 2.3 DATE 01/18/02)

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Date

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~~Corporate Technology~~ Technical Director Date

Proprietary Information Statement:

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TABLE OF CONTENTS

LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of soil samples for the analysis of certain metals by Graphite Furnace Atomic Absorption (GFAA), Flame Atomic Absorption (FLAA), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) as specified in SW846 Method 3050B.

1.2. Samples prepared by the protocols detailed in this SOP may be analyzed by ICP, ICP/MS, FLAA or GFAA for the elements listed in Table I (Appendix A). Other elements and matrices may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This method is not a total digestion, but will dissolve almost all metals that could become "environmentally available". By design, metals bound in silicate structures are not dissolved by this procedure, as they are not usually mobile in the environment. This SOP can be applied to metals in solids, sludges, wastes and sediments.

1.4. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

A representative 1 gram (wet weight) portion of sample is digested in nitric acid and hydrogen peroxide. The digestate is refluxed with hydrochloric acid for ICP or FLAA analysis. The digestates are then filtered and diluted to 100 mL/100 g.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

3.2. Total Metals: The concentration determined on an unfiltered sample following digestion. Note that this method is designed to determine the total *environmentally available* metals.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination.

4.3. Boron and silica from the glassware will grow into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric media.

4.7. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

Hydrochloric acid and nitric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

Nitric acid and hydrogen peroxide.

5.3.3. All heating of samples must be carried out in a fume hood.

5.4. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.10. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.11. Any and all accidents and spills must be reported to the lab supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, digestion block, steam bath or other heating source capable of maintaining a temperature of 90-99°C.

6.2. Calibrated thermometer that covers a temperature range of 0-200°C.

6.3. Griffin beakers of assorted sizes or equivalent.

6.4. Vapor recovery device (Watch glasses, ribbed or other device).

6.5. Whatman No. 41 filter paper or equivalent.

6.6. Funnels or equivalent filtration apparatus.

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 100 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repippetors or suitable reagent dispensers.

6.11. Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes.

6.12. Class A volumetric flasks.

6.13. pH indicator strips (pH range 0 - 6).

6.14. Plastic bottles.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom STL North Canton solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP LCS/MS spike solution: Prepare the ICP LCS/MS working spike solutions from custom stock standards to the final concentration listed in Table II. The working spike must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS solution must be made fresh every three months.

7.4. Working GFAA LCS/MS spike solution: Prepare the GFAA working LCS/MS spike solutions by diluting the custom stock solution (7.2) 200x. The working spike solution must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working GFAA LCS/MS solution must be made fresh every three months.

7.5. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom STL North Canton solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.6. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables II through IV (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and GFAA LCS and matrix spike preparations.

7.7. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.8. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.10. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.11. 30% Hydrogen peroxide (H_2O_2), reagent grade.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Soil samples do not require preservation but must be stored at 4 °C ± 2 °C until the time of analysis.

9. QUALITY CONTROL

Table V (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using Method 3050B the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements or verified as detailed in STL North Canton QA Policy QA-005. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL North Canton reporting limit.

9.1.2. Initial Demonstration Study- this requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (CORP-MT-0001, CORP-MT-0003).

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not counted towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be redigested.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be reprepparation and reanalysis of the batch. Tables II and III provide the details regarding the stock, working standards and final spike concentrations for ICP and GFAA. Refer to Section 7.3 or 7.4 for instructions on preparation of the aqueous LCS.

9.5.1. The LCS is prepared by spiking a 1mL or 1 g aliquot of reagent water with 2 mL of the working LCS/MS spike solution (7.3 or 7.4). The LCS is then processed as described in either Section 11.10.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives

(DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include reprepparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include reprepparation of samples unless the results indicate that a spiking error may have occurred. Tables II through IV provide the details regarding the stock, working standards and final matrix spike concentrations for ICP and GFAA. Refer to Sections 7.3 and 7.4 for instructions on preparation of the working matrix spike solutions.

9.6.1. The soil matrix spike sample is prepared by spiking a 1 g aliquot of a sample with 2mL of the working LCS/MS spike solution (7.3 or 7.4). The matrix spike sample is then processed as described in either Section 11.10.

9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC which may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Hotplate or block temperature must be verified daily for each unit used and must be recorded on either the metals preparation log or in a hotplate temperature logbook. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate. For block digestors, use a tube containing water.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. The heating procedures are carried out in a properly functioning hood.

11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample. The use of automatic label printing programs is recommended to reduce transcription errors (QuantIMS option).

11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project administrator for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

11.8. In some cases, both AA and ICP digests are required on each sample. It is recommended that both aliquots be weighed out and processed at the same time.

11.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.10. Preparation of Soils, Sediments and Sludges for Analysis by GFAA, ICP, ICP/MS and FLAA.

11.10.1. Mix sample thoroughly by stirring with a clean plastic or wooden spoon or spatula. Some project plans may require, when possible, transfer of the entire sample from the original container to butcher paper or a clean beaker, mixing thoroughly, then returning the sample to its original container.

11.10.2. For each digestion procedure required (i.e., ICP or GFAA), weigh a 1.0 portion of solid and record the exact weight to the nearest 0.01 g. A 2 g sample size may also be used if needed to meet the reporting limits.

11.10.3. Measure additional aliquots of the designated samples for the MS and MSD analyses.

11.10.4. Spike each of the MS and MSD aliquots with 2 mL of the working LCS/MS spiking solution (7.3 or 7.4).

11.10.5. Prepare a beaker for the method blank.

11.10.6. Prepare a beaker for the LCS. Add 2 mL of the working LCS/MS spiking solution (7.3 or 7.4).

11.10.7. Add 10 mL of 1:1 HNO_3 and mix the sample.

11.10.8. Heat sample to 95° ±4° C and reflux for 10 minutes without boiling, using a vapor recovery device.

Note: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY during any part of the digestion. Doing so will result in the loss of analyte and the sample must be reprepared.

11.10.9. Allow sample to cool, if necessary.

11.10.10. Add 5 mL of concentrated HNO_3 and replace vapor recovery device.

11.10.11. Reflux at 95° ±4° C for 30 minutes. (Add reagent water as needed to ensure that the volume of solution is not reduced to less than 5 mL.)

11.10.12. If brown fumes are observed, repeat step 11.10.10 until no more fumes are evolved.

11.10.13. Allow the samples to cool, if necessary.

11.10.14. Add approximately 2 mL of reagent water and 1 mL of 30 % H_2O_2. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

11.10.15. Replace the vapor recovery device and heat sample until effervescence subsides.

11.10.16. Allow the sample to cool, if necessary.

11.10.17. Continue adding 30% H_2O_2 in 1 mL aliquots with warming until effervescence is minimal or sample appearance is unchanged.

Note: Do not add more than a total of 10 mL of 30 % H_2O_2.

11.10.18. Continue heating at 95° ±4° C for 75 minutes until the volume is reduced to approximately 5-10 mL. Alternatively the sample may be heated for 2 hours.

11.10.19. If the sample is being prepared for ICP or FLAA analyses add 10 mL of concentrated HCl and reflux for an additional 10 minutes without boiling. This step is omitted for analysis by ICP-MS and GFAA

Note: Antimony and silver have poor solubility in dilute nitric acid solution. Therefore it is strongly recommended that these elements are determined by the ICP procedure that includes HCl as the final digestion acid.

11.10.20. Allow the sample to cool.

11.10.21. Wash down beaker walls and vapor recovery device with reagent water.

11.10.22. Filter sample through Whatman 41 filter paper or equivalent into a graduated cylinder or equivalent or a pre-weighed bottle. Other measuring bottles (for example, Corning Snap Seals™) may be used if their accuracy is documented and is better than ± 2%. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material

11.10.23. Dilute sample to 100 mL or 100g with reagent water. The sample is now ready for analysis.

Note: This SOP allows for samples to be weighed instead of measured volumetrically. This assumes the density of the diluted sample is close to 1.0 g/mL (See Section 17.1.2).

12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 20 % and the matrix spike duplicates should compare

within 20% RPD. Method blanks must meet the criteria specified in the determinative SOPs. The laboratory control samples should recover within 20% of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

15.2. Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996. Method 3050B.

16.2. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010B and Method 200.7.

16.3. CORP-MT-0003, Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.4. NC-MT-0002, Inductivcly Coupled Plasma-Mass Spectrometry, EPA Methods 6020 and 200.8.

16.5. QA-003, STL North Canton QC Program.

16.6. QA-004, Rounding and Significant Figures.

16.7. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants, as defined in the determinative SOPs, are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.2. This SOP allows for aqueous samples to be weighed instead of measured volumetrically. This assumes the density of the sample is close to 1.0 g/mL. Samples with large amounts of sediment or suspended solids, sludges, non-aqueous liquids must be processed volumetrically. Weighing samples directly into the digestion vessel minimizes the potential for cross contamination, offers improved accuracy over the use of graduated cylinders (comparable to volumetric flask accuracy), uses less glassware and is more efficient.

17.2. Modifications from previous SOP

17.2.1. ICP/MS has been added as an appropriate determinative technique.

17.2.2. The approved analyte list may be modified provided that additional elements meet the requirements in section 13.

17.2.3. Directions for digestion for set time periods rather than reduction to set volumes have been added.

17.2.4. The order of two steps in the digestion has been changed. (See section 11.10.20)

17.2.5. Definition of the method as determining total environmentally available metals has been added.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required supporting this SOP.

17.4. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst initials, matrix, prep type (ICP or GFAA).
- Sample ID; initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst initials.

Figure 1. Soil Sample Preparation (Section 11.10)

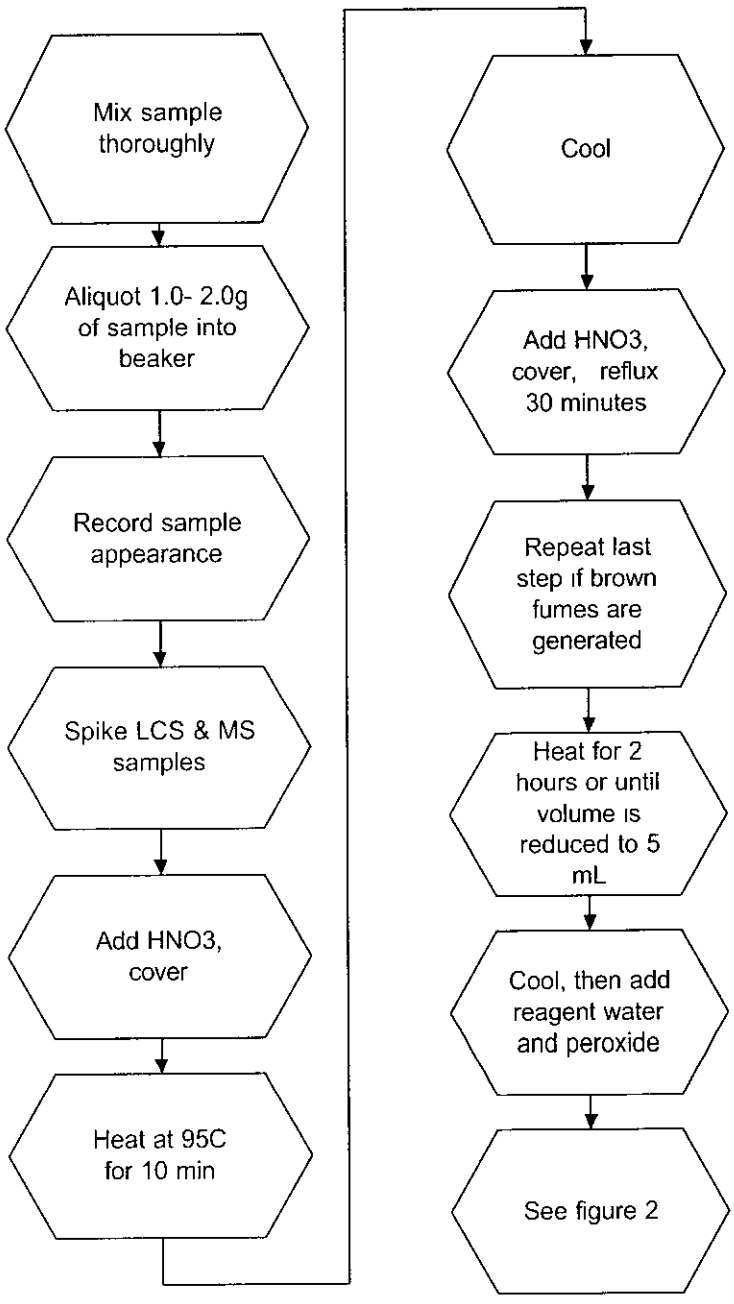
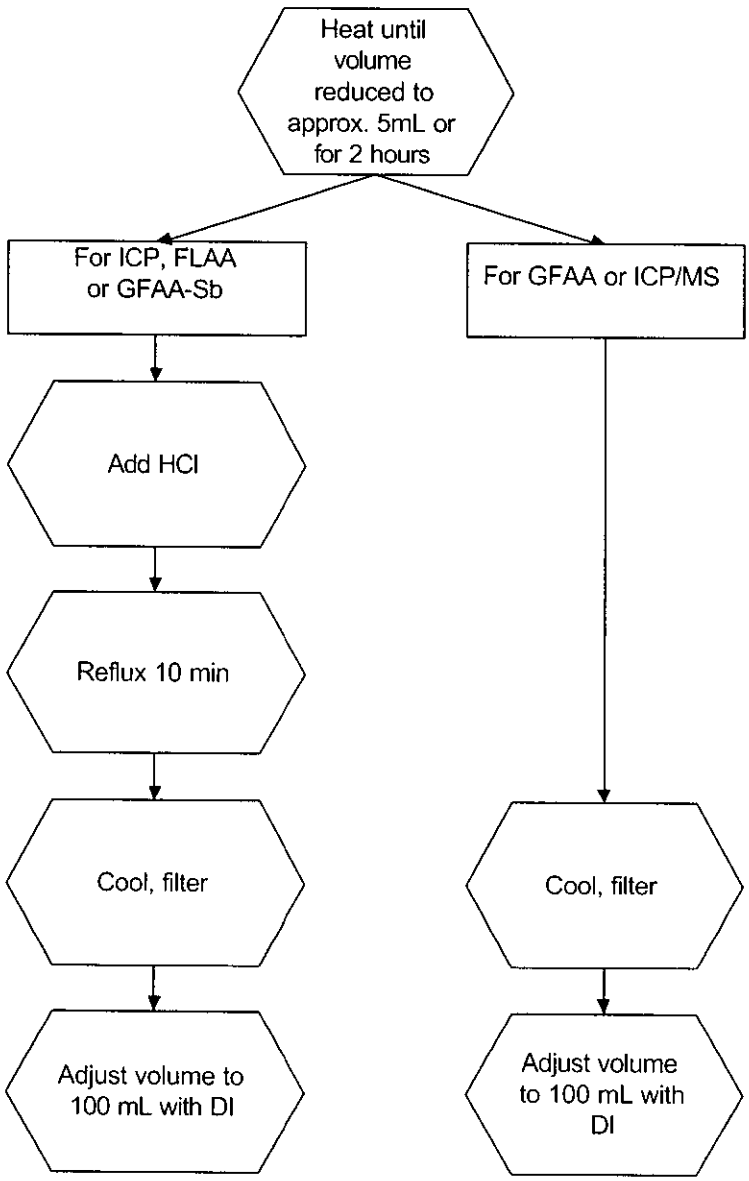


Figure 2. Soil Sample Preparation (continued)



APPENDIX A

TABLES

TABLE I. Method 3050A Approved Analyte List

ELEMENT	Symbol	CAS Number
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Potassium	K	7440-09-7
Selenium	Se	7782-49-2
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Thallium	Tl	7440-28-0
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

TABLE II. ICP and FLAA Soil Matrix Spike and Aqueous LCS Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/MS Level* (ug/L)	Soil MS Level ** (mg/Kg)
Aluminum	100	2000	200
Antimony	25	500	50
Arsenic	100	2000	200
Barium	100	2000	200
Beryllium	2.5	50	5
Cadmium	2.5	50	5
Calcium	2500	50000	5000
Chromium	10	200	20
Cobalt	25	500	50
Copper	12.5	250	25
Iron	50	1000	100
Lead	25	500	50
Lithium	50	1000	100
Magnesium	2500	50000	5000
Manganese	25	500	50
Molybdenum	50	1000	100
Nickel	25	500	50
Potassium	2500	50000	5000
Selenium	100	2000	200
Silver	2.5	50	5
Sodium	2500	50000	5000
Strontium	50	1000	100
Thallium	100	2000	200
Vanadium	25	500	50
Zinc	25	500	50
Boron	50	1000	100
Tin	100	2000	200
Titanium	50	1000	100

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 2.0 mL working spike (7.3) to 100 mL of sample.

** Final soil spike concentration based on the addition of 2.0 mL working spike (7.3) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE III. ICPMS Soil Matrix Spike and Aqueous LCS Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/MS Level* (ug/L)	Soil MS Level ** (mg/Kg)
Aluminum	100	1000	100
Antimony	10	100	10
Arsenic	10	100	10
Barium	10	100	10
Beryllium	10	100	10
Cadmium	10	100	10
Calcium	100	1000	100
Chromium	10	100	10
Cobalt	10	100	10
Copper	10	100	10
Iron	100	1000	100
Lead	10	100	10
Magnesium	100	1000	100
Manganese	10	100	10
Molybdenum	10	100	10
Nickel	10	100	10
Potassium	100	1000	100
Selenium	10	100	10
Silver	10	100	10
Sodium	100	1000	100
Strontium	10	100	10
Thallium	10	100	10
Vanadium	10	100	10
Zinc	10	100	10
Boron	10	100	10
Tin	10	100	10
Titanium	10	100	10
Zirconium	10	100	10

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.4) to 100 mL of sample.

** Final soil spike concentration based on the addition of 1.0 mL working spike (7.4) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE IV. GFAA Soil Matrix Spike and Aqueous LCS Spike Levels

ELEMENT	Stock LCS/MS Standard (mg/L)	Working LCS/MS Standard (ug/L)	Aqueous LCS/ MS Level * (ug/L)	Soil MS Level** (mg/Kg)
Arsenic	400	2000	40	4
Selenium	400	2000	40	4
Lead	400	2000	40	4
Thallium	400	2000	40	4
Antimony	400	2000	40	4
Cadmium	40	200	4	0.4
Chromium	100	500	10	1
Silver	50	250	5	0.5

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.5) to 50 mL of sample.

** Final soil spike concentration based on the addition of 2.0 mL working spike (7.5) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE V. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze samples.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	See Corrective Action for Matrix Spike.

APPENDIX B

CONTAMINATION CONTROL GUIDELINES

APPENDIX B. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or latex gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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Implementation Date: 4/25/03

SOP No. CORP-IP-0003NC
Revision No. 1.4
Revision Date: 02/19/03

STL STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF AQUEOUS SAMPLES BY SW846 AND MCAWW 200 SERIES METHODS

(Supersedes: Revision 1.3 Dated 09/25/01)

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Date

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TABLE OF CONTENTS

LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of aqueous samples for the analysis of certain metals by Graphite Furnace Atomic Absorption (GFAA), Flame Atomic Absorption (FLAA), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) using the MCAWW 200 series methods (NPDES) and SW846 Methods 3005A, 3010A, 3020A and 7060A/7740 (RCRA).

1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables I and II (Appendix A) and the applicable determinative methods are illustrated by Figures 6 and 7 (Section 17). Additional elements may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This SOP provides procedures applicable to the preparation of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, certain aqueous sludges, wastes, and biological tissues, and leachates/extracts.

1.4. SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by FLAA, ICP and GFAA (antimony only).

1.5. MCAWW Method 200.7 Section 9.4 is used to prepare surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by ICP.

1.6. SW-846 Method 3010A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals analysis by FLAA or ICP.

1.7. MCAWW Method 200.7 Section 9.3 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by ICP.

1.8. SW-846 Method 3020A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals by GFAA, or ICP/MS.

1.9. MCAWW Method 200.0 Section 4.1.3 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by GFAA.

1.10. MCAWW Method 200.0 Section 4.1.4 is used to surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by GFAA.

1.11. SW-846 Methods 7060A and 7740, respectively, contain the procedure for the preparation of aqueous samples for arsenic and selenium.

1.12. MCAWW Methods 206.2 and 270.2, respectively, contain the procedure for the preparation of aqueous samples for arsenic and selenium.

1.13. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators do require digestion of dissolved samples and this must be clarified before project initiation.

2. SUMMARY OF METHOD

2.1. Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP Spectroscopy

2.1.1. A representative aliquot of sample is heated with nitric and hydrochloric acids and substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.2. Method 3010A / Method 200.7 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy

2.2.1. A representative aliquot of sample is refluxed with nitric acid. After the digestate has been reduced to a low volume, it is refluxed with hydrochloric acid, filtered (if necessary) and brought up to volume.

2.3. Method 3020A / Method 200.0 Section 4.1.3 - Preparation for Total Metals for Analysis by GFAA Spectroscopy and ICP/MS.

2.3.1. A representative aliquot of sample is refluxed with nitric acid. After the digestate has been reduced to a low volume, it is cooled, filtered (if necessary) and brought up to volume.

2.4. Methods 7060A/206.2 and Methods 7740/270.2 - Preparation for Arsenic/Selenium Analysis by GFAA

2.4.1. A representative aliquot of sample is heated with nitric acid and peroxide until the digestate has been reduced to a low volume. The sample is cooled, filtered (if necessary) and brought up to volume.

2.5. Method 200.0 Section 4.1.4 - Total Recoverable GFAA Preparation (NPDES)

A representative aliquot of sample is heated with nitric acid and until the digestate has been reduced to a low volume. The sample is cooled, filtered (if necessary) and brought up to volume.

3. DEFINITIONS

Additional definitions of terms used in this SOP may be found in the glossary of the LQM.

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix B for additional contamination control guidelines.

4.3. Boron and silica from the glassware will migrate into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.7. Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample.

4.8. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid and nitric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. All sample digestions, including cooling of digestates, must be carried out in a fume hood.

5.4. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.8. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.9. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.10. Any and all accidents and spills must be reported to the lab supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, digestion block or other adjustable heating source capable of maintaining a temperature of 95°C (± 4).

6.2. Calibrated thermometer that covers a temperature range of 0-200°C.

6.3. Griffin beakers of assorted sizes or equivalent.

6.4. Watch glasses, ribbed or equivalent.

6.5. Whatman No. 4 filter paper or equivalent.

6.6. Funnels or equivalent filtration apparatus.

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 50 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repipetors or suitable reagent dispensers.

6.11. Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes.

6.12. Class A volumetric flasks.

6.13. pH indicator strips (pH range 0 - 6).

6.14. Plastic digestate storage bottles.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP LCS/MS spike solution: Prepare the ICP LCS/MS working spike solution from custom stock standards to the final concentration listed in Table III. The working

spike must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS solution must be made fresh every three months.

7.4. Working GFAA LCS/MS spike solution: Prepare the GFAA working LCS spike solution by diluting the custom stock solution (7.2) 200x. The working spike solution must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working GFAA LCS solution must be made fresh every three months.

7.5. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.6. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom STL solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.7. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables III and IV(Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and GFAA LCS and matrix spike preparations.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.9. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.10. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.11. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.12. 30% Hydrogen peroxide (H_2O_2), reagent grade.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. For dissolved metals analysis, the samples should be filtered through a 0.45 um filter prior to preservation. Filtration must be done in the field or within 24 hours of collection.

Note: If a sample being analyzed for dissolved metals is found to contain sediment the analyst should contact their supervisor or group leader. The client should be notified of the problem to decide how to treat the sample.

9. QUALITY CONTROL

Table VI (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using any method contained within this SOP the following requirements must be met:

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDL's must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in STL QA Policy QA-005. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to

extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (CORP-MT-0001, CORP-MT-0003).

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS) are not included in the sample count for determining the size of a preparation batch. MS/MSD are not included in the sample count unless there are multiple sets of MS/MSD per batch. In other words, the first MS/MSD are not counted; all additional MS and MSDs are counted as samples.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs; the blank and all associated samples in the batch must be redigested.

9.4.1. Aqueous method blanks are prepared by taking 50 mL or 50 g of reagent water through the appropriate procedure as described in Section 11.

9.4.2. TCLP method blanks are prepared by taking 50 mL or 50 g of leachate fluid through the appropriate procedure as described in Section 11.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried

through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be reprepparation and reanalysis of the batch. Refer to Section 7.3 and 7.4 for instructions on preparation of the aqueous LCS spike solution.

9.5.1. The aqueous LCS is prepared by spiking a 50 mL aliquot of reagent water with 1.0 mL of the working LCS/MS spike solution (7.3 or 7.4). The LCS is then processed through the appropriate procedure as described in Section 11.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include reprepparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include reprepparation of samples unless the results indicate that a spiking error may have occurred.

9.6.1. The aqueous matrix spike sample is prepared by spiking a 50 mL aliquot of a sample with 1.0 mL of the working LCS/MS spike solution (7.3 or 7.4). The matrix spike sample is then processed as described in Section 11.

9.6.2. The TCLP matrix spike sample is prepared by spiking a 50 mL aliquot of a leachate with 0.5 mL of the working TCLP spike solution (7.5). The matrix spike sample is then processed as described in Section 11.

NOTE: The TCLP matrix spike must be added prior to preservation of the leachate.

9.6.3. If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC that may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

10. CALIBRATION AND STANDARDIZATION

10.1 Hotplate temperature must be verified daily for each hotplate used and must be recorded on either the metals preparation log or in a hotplate temperature logbook. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. All digestion procedures must be carried out in a properly functioning hood.

11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample.

11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project manager for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

11.8. In most cases, both AA and ICP digests are required on each sample. It is recommended that both aliquots be measured out and processed at the same time.

11.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.10. The following procedure must be followed for all aqueous sample preparations:

11.10.1. Measure sample pH with pH paper on a separate aliquot of sample.

Note: If the sample pH is > 2 pH units, the client must be notified of the anomaly.

Note: If sample pH has already been verified and documented in sample receipt this step may be omitted.

11.10.2. Mix sample by shaking the container.

11.10.3. Measure and transfer 50 mL or 50 g of the sample into a beaker.

Note: This SOP allows for samples to be weighed instead of measured volumetrically.

11.10.4. Measure two extra aliquots of sample selected for the MS/MSD analysis. Spike each aliquot with the appropriate spiking solutions (7.3-7.5,9.6).

11.10.5. Measure and transfer 50 mL of reagent water into a beaker for the method blank.

11.10.6. Measure and transfer 50 mL of reagent water into a beaker for the LCS and add the appropriate spiking solutions (7.3-7.5,9.6).

11.11. Proceed to the appropriate Section for the desired method as follows:

Method 3005A or Method 200.7 Section 9.4	11.12
Method 3010A or Method 200.7 Section 9.3	11.13
Method 3020A or Method 200.0 Section 4.1.3	11.14
Method 7060A/7740 or Method 206.2/270.2	11.15
Method 200.0 Section 4.1.4	11.16

11.12. **Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP (See Figures 1, 6 and 7)**

11.12.1. To the sample beaker, add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl.

11.12.2. Cover with ribbed watch glass.

11.12.3. Heat at 95°C (± 4) until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.12.4. Cool the beaker in a fume hood.

11.12.5. Wash down beaker walls and watch glass with reagent water.

11.12.6. Filter sample, if insoluble materials are present, through Whatman 4 filter paper that has been pre-rinsed with dilute nitric acid.

Note: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.12.7. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.12.8. Adjust the final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis

11.13. **Method 3010A / Method 200.7 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy (See Figures 2, 6 and 7)**

11.13.1. To the sample beaker, add 3.0mL of concentrated HNO_3.

11.13.2. Cover with ribbed watch glass.

11.13.3. Place beaker on hotplate 95°C (± 4) and evaporate for 4-5 hours or to low volume of 15-20 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.13.4. If necessary, add another 1.5 ml portion of concentrated HNO_3 and re-cover the beaker. Reflux 15 minutes.

11.13.5. Add 5 mL of 1:1 HCl.

11.13.6. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue. Cool in a fume hood.

11.13.7. Wash down beaker walls and watch glass with reagent water.

11.13.8. Filter sample, if insoluble materials are present, through Whatman 4 filter paper.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.13.9. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.13.10. Adjust final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis.

11.14. **Method 3020A / Method 200.0 Section 4.1.3 - Preparation for Total Metals Analysis by GFAA or Total Recoverable Metals by ICPMS (See Figures 3, 6 and 7)**

11.14.1. To the sample beaker, add 1.5 mL of concentrated HNO_3.

11.14.2. Cover with ribbed watch glass.

11.14.3. Place beaker on hotplate 95°C (± 4) and evaporate to low volume of 15-20 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.14.4. If necessary, add another 1.5 mL portion of concentrated HNO_3. Recover, and reflux 15 minutes. Cool the beaker in a fume hood.

11.14.5. Filter sample, if insoluble materials are present, through Whatman 4 filter paper.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.14.6. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.14.7. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.15. **Method 7060A/7740 and Method 206.2/270.2 - Preparation for Arsenic and Selenium Analysis by GFAA (See Figures 4, 6 and 7)**

11.15.1. To the sample beaker, add 1 mL of 30 % H_2O_2 and 1.0 mL of 1:1 HNO_3.

11.15.2. Heat, until the digestion is complete, at 95°C (± 4) or until the volume has been reduced to 15-20 mL.

11.15.3. Cool beaker.

11.15.4. Filter sample, if insoluble materials are present, through Whatman 4 filter paper that has been pre-rinsed with dilute nitric acid.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.15.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.15.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.16. **Method 200.0 Section 4.1.4 - Preparation for Total Recoverable GFAA Analyses. (See Figures 5 and 7)**

11.16.1. To the sample beaker, add 1.0 mL of 1:1 HNO_3.

11.16.2. Heat, until the digestion is complete, at 95°C (± 4) or until the volume has been reduced to 15 - 20 mL.

11.16.3. Cool beaker.

11.16.4. Filter sample, if insoluble materials are present, though Whatman 4 filter paper.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.16.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.16.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 20 % and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in determinative SOPs. The laboratory control samples should recover within 20% of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The facility EH & S coordinator should be contacted if additional information is required.

15.2. Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, Revision 1, July 1992. Methods 3005A, 3010A, 3020A, 7060A and 7740A.

16.2. Methods for the Chemical Analysis of Water and Waste (MCAWW), 1983.

16.3. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010A and Method 200.7.

16.4. CORP-MT-0003, Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.5. QA-003, STL QC Program.

16.6. QA-004, Rounding and Significant Figures.

16.7. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference methods.

17.1.1. Modifications applicable to SW-846 reference methods.

17.1.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.1.2. The referenced methods as well as Table 3-1 of SW-846 refer to the use of a 100 mL aliquot for digestion. This SOP requires the use of a 50 mL sample size to reduce waste generation. The use of reduced sample volumes are supported in EPA's document "Response to Public

Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document stated "flexibility to alter digestion volumes is addressed and "allowed" by the table (3-1) and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..." EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology." Additionally, in written correspondence from the Office of Solid Waste, Olliver Fordham stated " As a "representative sample" can be assured, scaling causes no loss of precision and accuracy in the analysis."

17.1.2. Modifications Specific to Method 3010A

17.1.2.1. Section 11.13.7 of this SOP requires the sample be reduced to a volume of 15 - 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.2.2. The scope of 3010A has been expanded to include silver based on comparison studies with 7760A. Method 3010A consistently demonstrated improved accuracy and precision over Method 7760A in the matrices tested (reagent water, surface water and TCLP leachate) up to a concentration of 1 ppm silver.

17.1.3. Modifications Specific to Method 3020A

17.1.3.1. Section 11.14.3 of this SOP requires the sample be reduced to a volume of 15 - 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.4. Modifications Specific to Method 7060A/7740

17.1.4.1. Methods 7060A and 7740A incorporate the use of a two step dilution to accommodate the addition of a nickel nitrate modifier. This SOP performs the dilution directly in one step and omits the addition of the modifier. The modifier is added automatically at the instrument by direct injection into the furnace.

17.1.5. Modifications Specific to MCAWW Methods

It was determined by technical review that several of the MCAWW methods were equivalent to the SW-846 methods and therefore were combined under the scope of this SOP as described in Section 11.0. The nature of the differences were deemed insignificant in regards to the amount of acid added and the evaporative volume based on the flexibility allowed by the methods (i.e., add additional acid as required) and the subjective wording of the methods (i.e., evaporate to near dryness vs. an exact volume).

17.2. Modifications from previous SOP

17.2.1. Added ICP/MS to the digestion procedures.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst name, matrix, prep type (ICP or GFAA), SOP reference.
- Sample ID; initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst Signature.
- Reviewer's Signature and date.

Figure 1. Method 3005A / Method 200.7 Section 9.4 (Section 11.12)

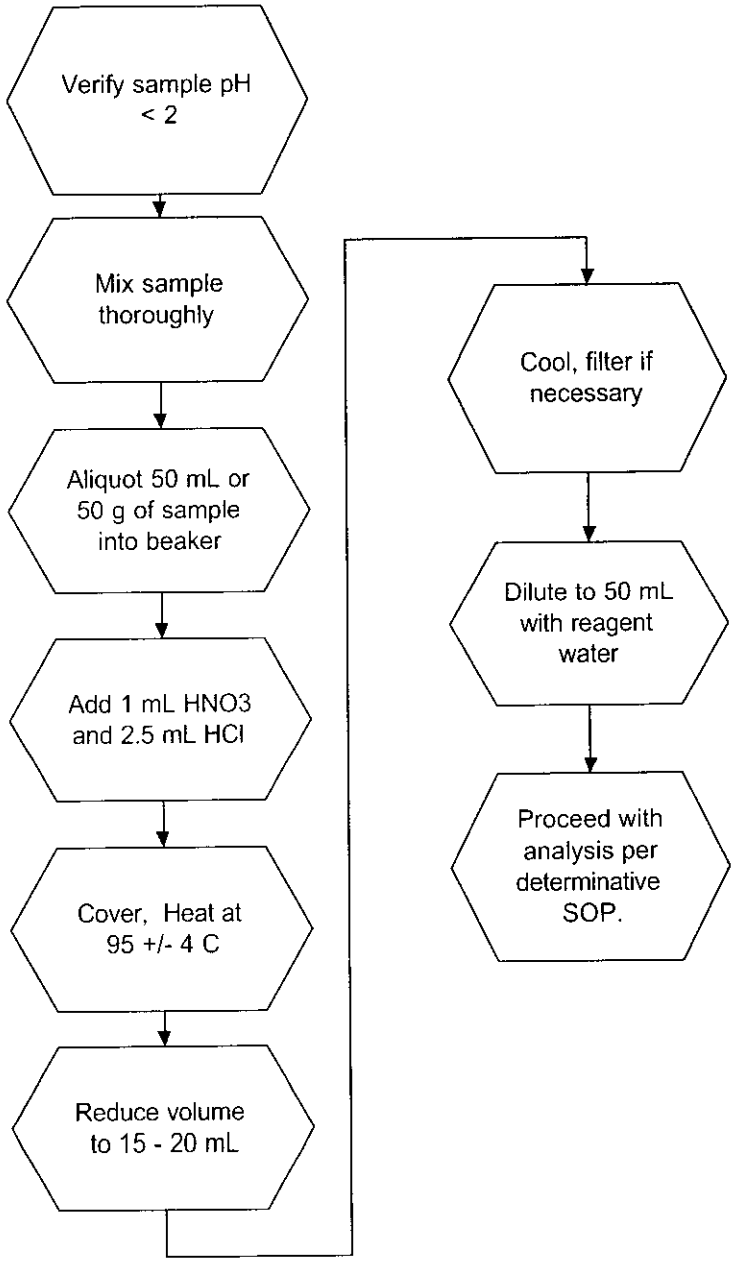


Figure 2. Method 3010A / Method 200.7 Section 9.3 (Section 11.13)

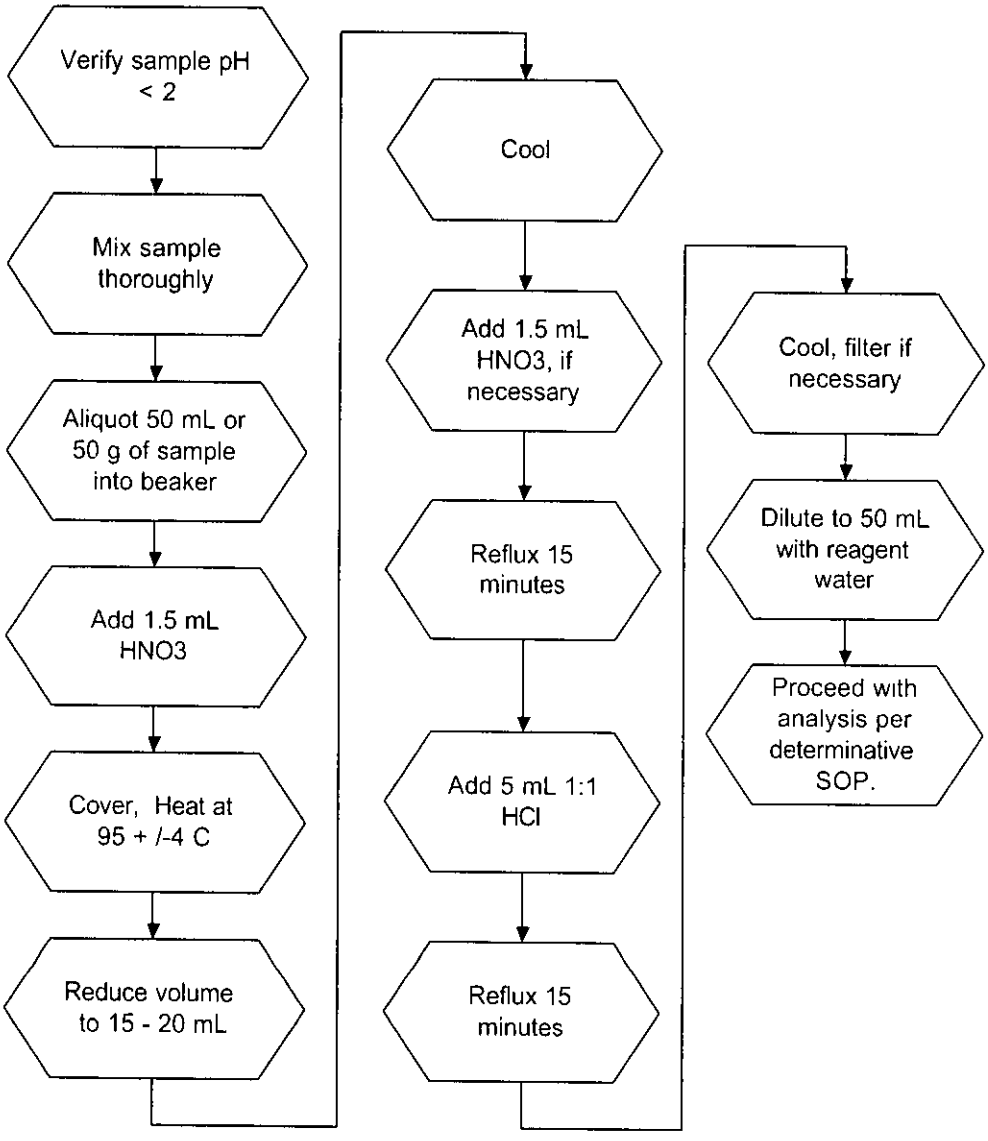


Figure 3. Method 3020A / Method 200.0 Section 4.1.3 (Section 11.14)

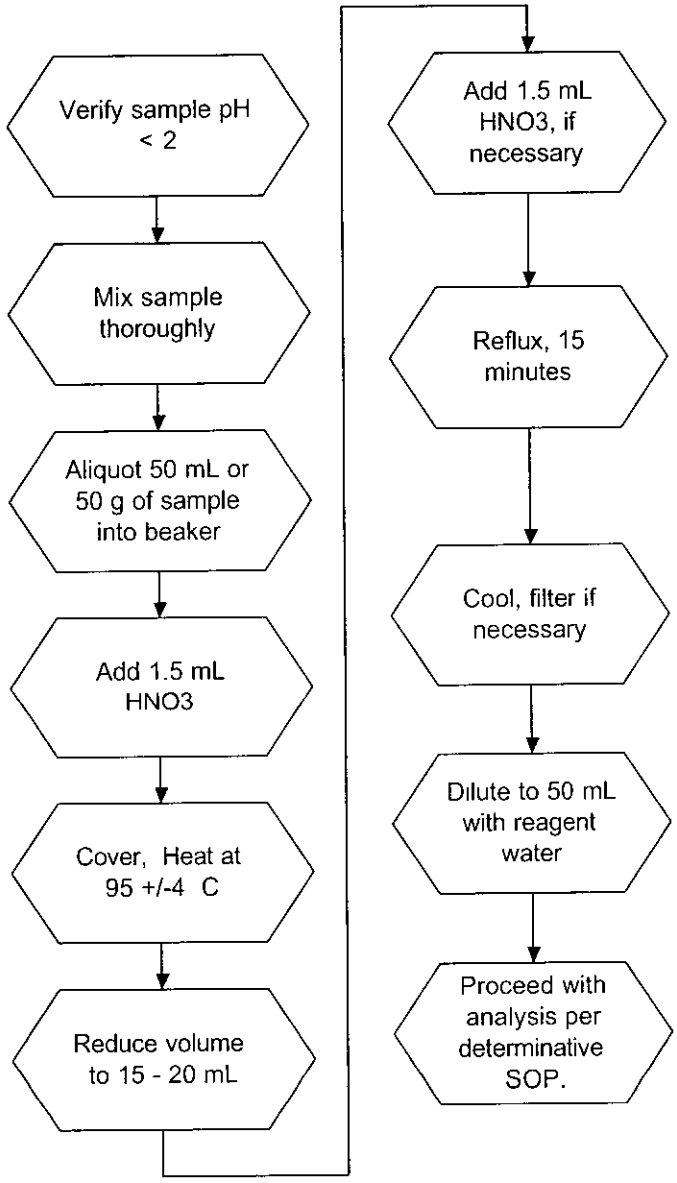


Figure 4. Method 7060A/7740A and Method 206.2/270.2 (Section 11.15)

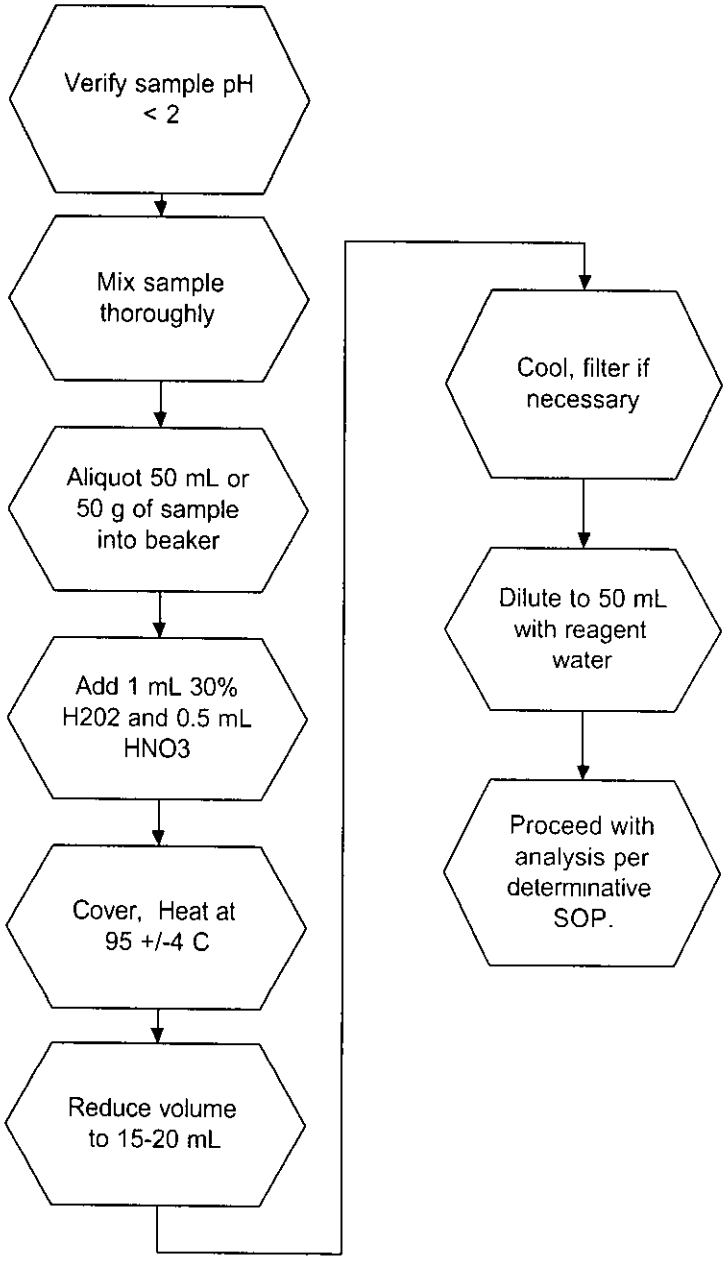


Figure 5. Method 200.0 Section 4.1.4 (Section 11.16)

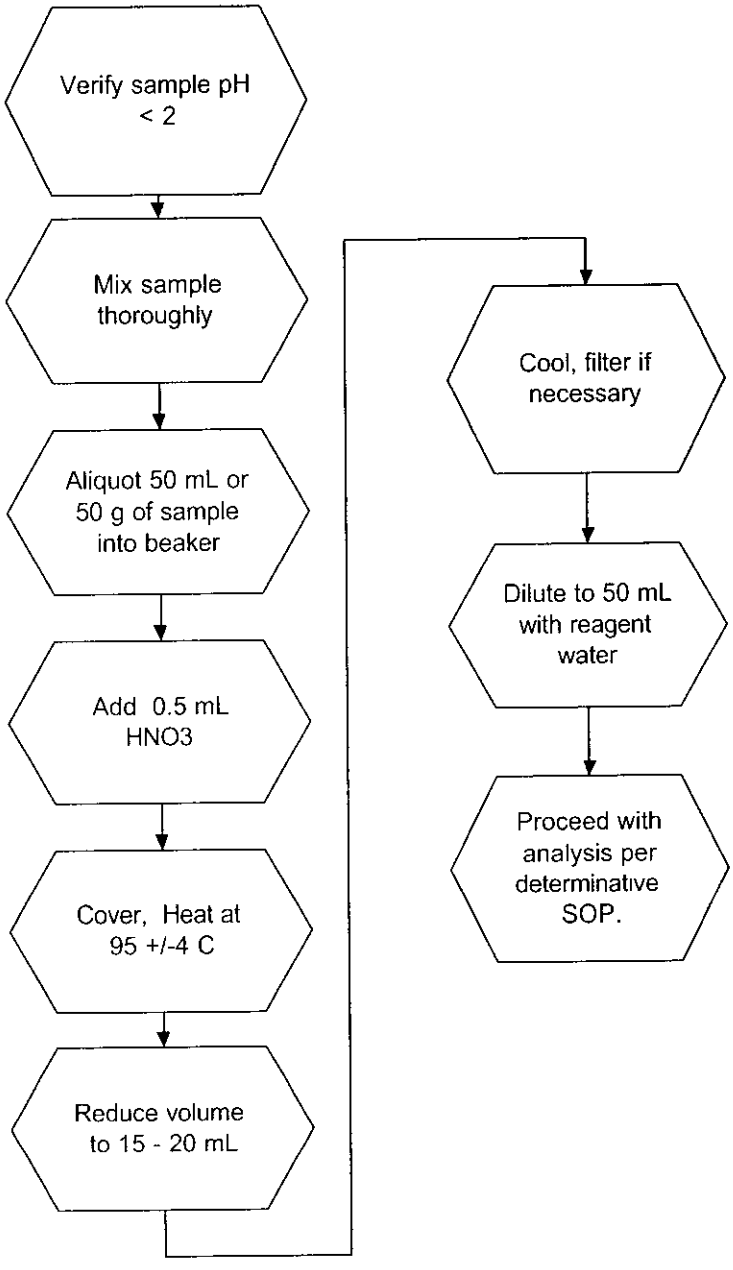
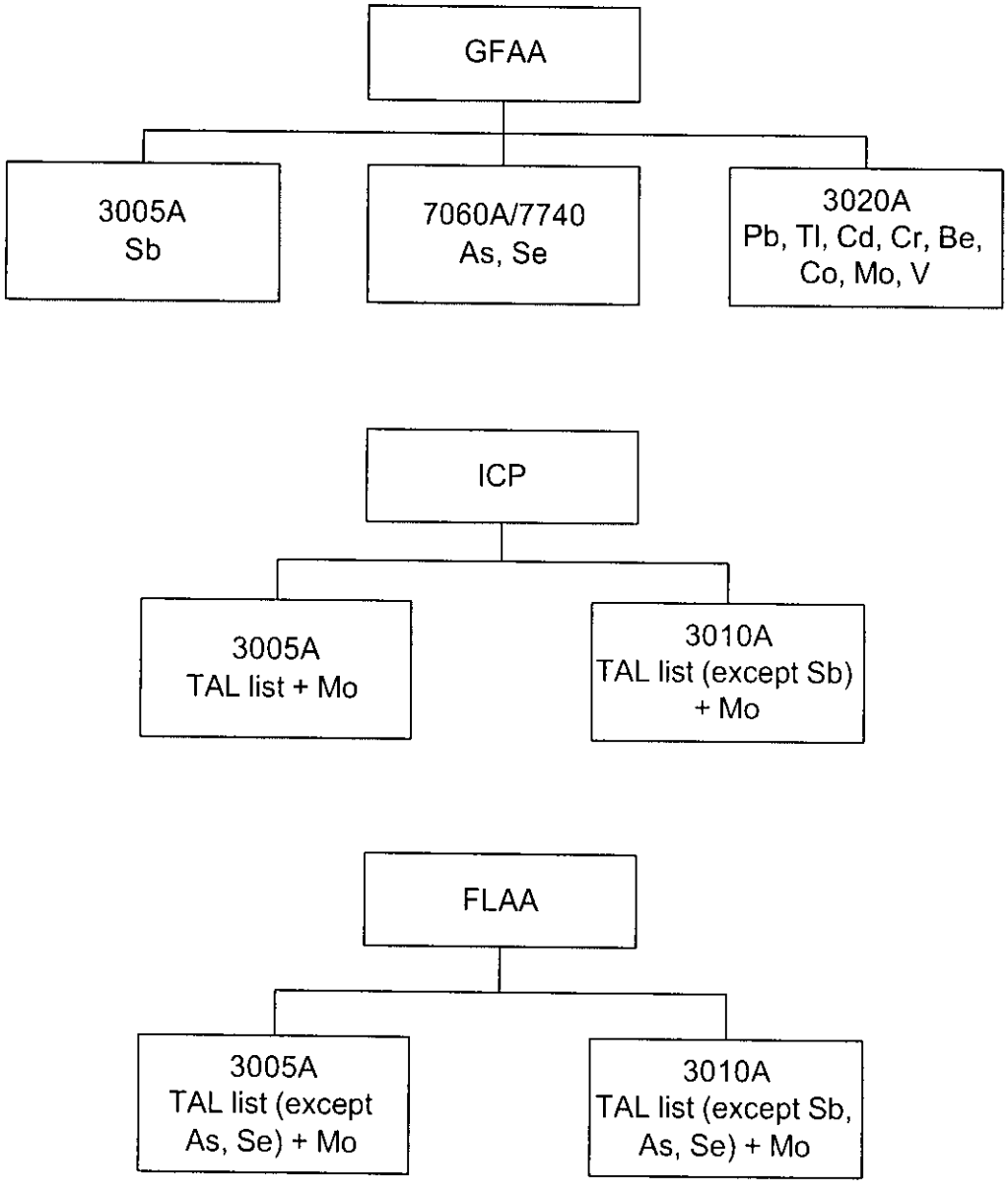
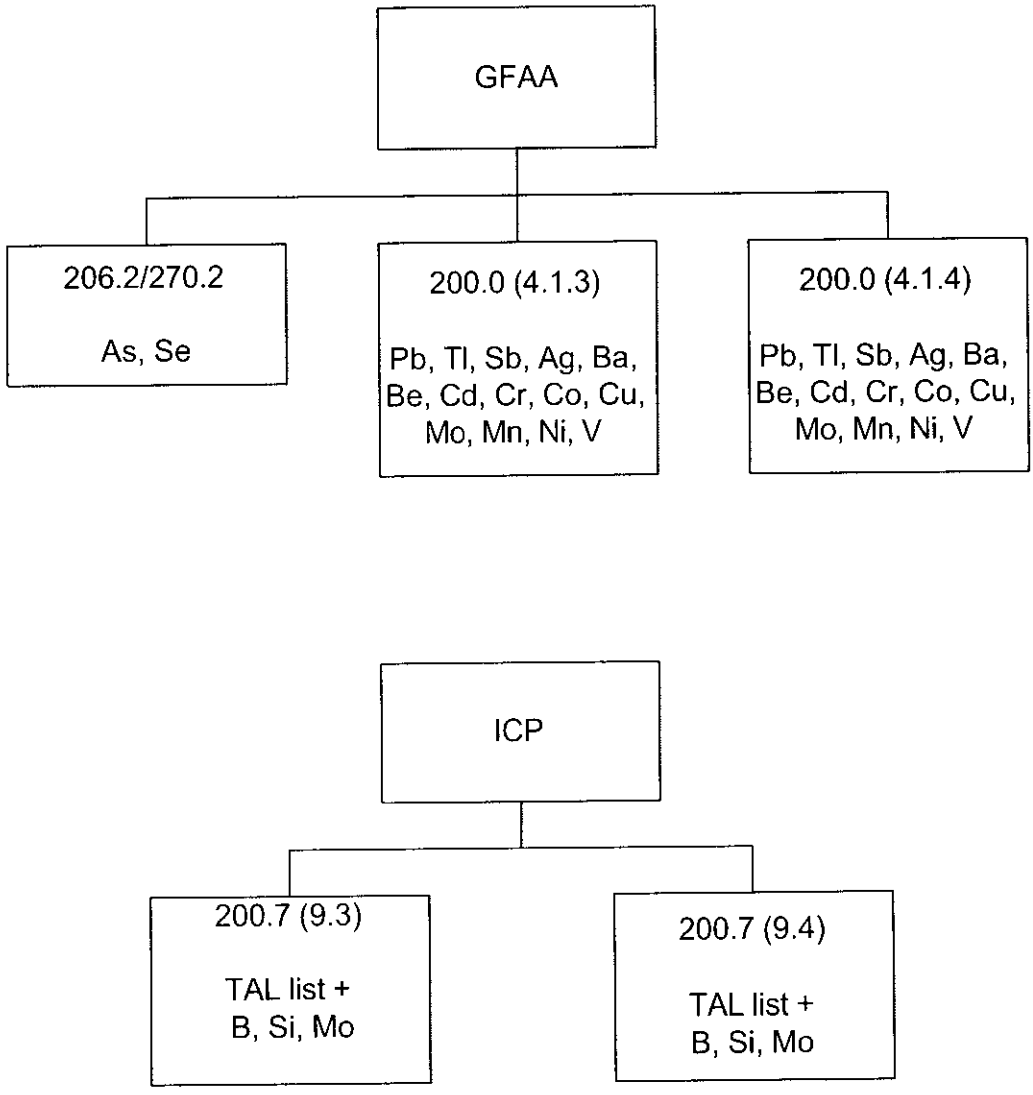


Figure 6. Overview of SW846 Aqueous Preparation Methods by Determinative Method



TAL list: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

Figure 7. Overview of MCAWW Aqueous Preparation Methods by Determinative Technique



TAL list: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

APPENDIX A

TABLES

TABLE I. Approved Preparation Method Analytes - SW846

ELEMENT	Symbol	CAS Number	3005A	3010A	3020A	7060A 7740
Aluminum	Al	7429-90-5	X	X		
Antimony	Sb	7440-36-0	X			
Arsenic	As	7440-38-2	X	X		X
Barium	Ba	7440-39-3	X	X		
Beryllium	Be	7440-41-7	X	X	X	
Cadmium	Cd	7440-43-9	X	X	X	
Calcium	Ca	7440-70-2	X	X		
Chromium	Cr	7440-47-3	X	X	X	
Cobalt	Co	7440-48-4	X	X	X	
Copper	Cu	7440-50-8	X	X		
Iron	Fe	7439-89-6	X	X		
Lead	Pb	7439-92-1	X	X	X	
Magnesium	Mg	7439-95-4	X	X		
Manganese	Mn	7439-96-5	X	X		
Molybdenum	Mo	7439-98-7	X	X	X	
Nickel	Ni	7440-02-0	X	X		
Potassium	K	7440-09-7	X	X		
Selenium	Se	7782-49-2	X	X		X
Silver	Ag	7440-22-4	X	X		
Sodium	Na	7440-23-5	X	X		
Thallium	Tl	7440-28-0	X	X	X	
Vanadium	V	7440-62-2	X	X	X	
Zinc	Zn	7440-66-6	X	X		

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE II. Approved Preparation Method Analytes - NPDES

ELEMENT	Symbol	CAS Number	200.7 (9.4)	200.7 (9.3)	200.0 (4.1.4)	200.0 (4.1.3)	206.2 270.2
Aluminum	Al	7429-90-5	X	X			
Antimony	Sb	7440-36-0	X	X	X	X	
Arsenic	As	7440-38-2	X	X			X
Boron	B	7440-42-8	X	X			
Barium	Ba	7440-39-3	X	X	X	X	
Beryllium	Be	7440-41-7	X	X	X	X	
Cadmium	Cd	7440-43-9	X	X	X	X	
Calcium	Ca	7440-70-2	X	X			
Chromium	Cr	7440-47-3	X	X	X	X	
Cobalt	Co	7440-48-4	X	X	X	X	
Copper	Cu	7440-50-8	X	X	X	X	
Iron	Fe	7439-89-6	X	X	X	X	
Lead	Pb	7439-92-1	X	X	X	X	
Magnesium	Mg	7439-95-4	X	X			
Manganese	Mn	7439-96-5	X	X	X	X	
Molybdenum	Mo	7439-98-7	X	X	X	X	
Nickel	Ni	7440-02-0	X	X	X	X	
Potassium	K	7440-09-7	X	X			
Selenium	Se	7782-49-2	X	X			X
Silicon	Si	7631-86-9	X	X			
Silver	Ag	7440-22-4	X	X	X	X	
Sodium	Na	7440-23-5	X	X			
Thallium	Tl	7440-28-0	X	X	X	X	
Vanadium	V	7440-62-2	X	X	X	X	
Zinc	Zn	7440-66-6	X	X			

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE III. ICP and FLAA Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/ MS Level * (ug/l)
Aluminum	100	2000
Antimony	25	500
Arsenic	100	2000
Barium	100	2000
Beryllium	2.5	50
Cadmium	2.5	50
Calcium	2500	50000
Chromium	10	200
Cobalt	25	500
Copper	12 5	250
Iron	50	1000
Lead	50	500
Magnesium	2500	50000
Manganese	25	500
Molybdenum	50	1000
Nickel	25	500
Phosphorous	500	10000
Potassium	2500	50000
Selenium	100	2000
Silver	2.5	50
Sodium	2500	50000
Thallium	100	2000
Vanadium	25	500
Zinc	25	500
Boron	50	1000
Tin	100	2000
Titanium	50	1000

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.3) to 50 mL of sample.

TABLE IV. GFAA Matrix Spike and Aqueous LCS Spike Levels

ELEMENT	Stock LCS/MS Standard (mg/L)	Working LCS/MS Standard (ug/L)	Aqueous LCS/ MS Level * (ug/l)
Arsenic	400	2000	40
Selenium	400	2000	40
Lead	400	2000	40
Thallium	400	2000	40
Antimony	400	2000	40
Cadmium	40	200	4
Chromium	100	500	10
Silver	50	250	5

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.4) to 50 mL of sample.

TABLE V. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)*
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 0.5 mL working spike (7.4) to 50 mL of sample

TABLE VI. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze samples associated with the method blank.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	See Corrective Action for Matrix Spike.

APPENDIX B

CONTAMINATION CONTROL GUIDELINES

APPENDIX B. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

8771731

STL

SOP No. COI-GC-005
Revision No. 4
Revision Date: 05/21/04
Effective Date: 06/04/04
Page: 1 of 19

STANDARD OPERATING PROCEDURE

TITLE: SAMPLE PREPARATION AND THE DETERMINATION OF DISSOLVED GASES IN WATER BY USING GC HEADSPACE EQULIBRATION TECHNIQUE (EPA RSKSOP-175 MODIFIED)

(SUPERSEDES: REV. 3)

Prepared by: David Kammerer

Reviewed by: Technical Specialist, Lerylina Yabut

Approved by: Quality Assurance Manager, Linda Scharpenberg

Approved by: Environmental Health and Safety Coordinator, Linda Scharpenberg

Approved by: Laboratory Director, Elizabeth A. Winger

TABLE OF CONTENTS

1. SCOPE AND APPLICATION

1.1. This method is applicable to the preparation of water samples and analysis of the prepared headspace to quantify part-per-million to percent levels of dissolved gases in the water sample. Although this method is specifically for the determination of Methane, Ethane, and Ethene, it may also be modified for Nitrogen, Oxygen, Carbon Dioxide, and Carbon Monoxide. This procedure is based on a non-promulgated method, EPA RSKSOP 175.

1.2. This method is restricted to use by or under the supervision of analysts experienced in sample preparation and in the use of gas chromatography and the interpretation of chromatograms

2. SUMMARY OF METHOD

2.1. A water sample is collected in a 40ml Voa vial, free of headspace, and capped using a Teflon-faced septum and crimp or screw-on cap, or equivalent, of the appropriate size to fit the bottle.

2.2. A headspace is generated in the laboratory by replacing 10 percent of the water sample with high purity Helium.

2.3. The sample bottle is agitated for 5 minutes and a sample is taken of the headspace and injected onto a gas chromatographic system where the gaseous components of interest are separated and detected by flame ionization detector or thermal conductivity detector.

2.4. By using Henry's Law, the headspace concentration of the gas, the bottle volume and the temperature of the sample, the concentration of the dissolved gas in the original water sample can be determined.

3. DEFINITIONS

3.1. Batch - An Analytical Batch is defined as a set of up to 20 client samples of the same matrix processed using the same procedures and reagents within the same time period. A batch must contain a Laboratory Control Sample (LCS), a Laboratory Control Sample Duplicate (LCSD), and a Method Bank. Using this method, the first CCV analysis will normally start a new analytical batch.

3.2. The Quality Control Batch must contain a Laboratory Control Sample (LCS), a Laboratory Control Sample Duplicate (LCSD) and a Method Bank.

3.3. Method Blank - A Method Blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The Method Blank is used to identify any background interference or contamination of the analytical system that may lead to the reporting of elevated concentration levels or false positive data.

3.4. Laboratory Control Samples (LCS/LCSD) - Laboratory Control Samples are laboratory-generated samples used to monitor the laboratory's day-to-day performance. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

3.5. Method Detection Limits - The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from seven replicate analysis of low level standards in a typical representative matrix.

3.6. Ambient Air (Room Air) - "Room air" is defined as containing 78.08% v/v Nitrogen, 20.946% v/v Oxygen, and 0.934% v/v Argon.

4. INTERFERENCES

4.1. This system is relatively free of interferences due to specificity of the multiple columns used and the back-flush capabilities of the system. Compounds of interest are well separated and there are no major baseline upsets at expected retention times to complicate correct peak integration.

4.2. Ambient air (in the laboratory) contains approximately 400ppmv Carbon Dioxide and several ppmv of Methane. These concentrations should be considered variable and be taken into consideration whenever "room air" is used as a standard.

4.3. Argon naturally occurs in ambient air at 0.934 percent, and co-elutes with Oxygen.

4.4. The referenced methods note that water vapor can interfere with the chromatic baseline. STL Los Angeles' choice of columns and back-flush technique after elution of target compounds minimizes this problem.

4.5. Hydrochloric Acid used for preservation of the samples has been shown to contribute to the Carbon Dioxide result, either through chemical interaction with the sample or from Carbon Dioxide contained in the HCL. Ideally, samples analyzed for Carbon Dioxide should be unpreserved.

4.6. This method is dependent on sample volumes, so final results are affected by samples containing large amounts of sediment or solid material.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Employees must abide by the policies and procedures in the Corporate Safety Manual, Lab Specific Addendum to the CSM, and this document.

5.3. Specific Safety Concerns and Requirements

5.3.1. MAPA Blue Grip gloves should be worn when handling the VOA vials.

5.3.2 Hydrogen is flammable

5.3.3 All safety issues involving compressed gas cylinders should be followed. All compressed gas cylinders must be securely fastened to a bench or wall.

5.3.4 Tedlar bags may be used for standard preparation. These must be handled with care and must not be over pressurized to prevent them from rupturing. Make sure the valves are closed tightly when not in use.

5.3.5 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit

5.4. Primary Materials Used

5.4.1. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDSs) maintained in the laboratory. Analysts and Technicians need to be familiar with the information contained in the applicable MSDS's before beginning work on this method. The following specific hazards are known:

Material (1)	Hazards	OSHA Exposure Limit (2)	Signs and symptoms of exposure/Unusual Hazards
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

5.5. Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported immediately to a Supervisor

6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph - capable of temperature programming for the oven and automatic multiple valve control, and equipped with thermal conductivity and flame ionization detectors (Varian 3400)

6.2. Custom valving and reduction catalyst housing (Valco Instruments and Lotus Consulting)

6.3. Tube oven for oxidation catalyst capable of 600 degrees C (Lindberg or equivalent)

6.4. Chromatographic grade stainless steel tubing and stainless steel plumbing fittings

6.5. Stainless steel chromatographic columns - Tenax 1/8" x 4', Chromasorb 106 1/8" x 6', Mol Seive 5A 1/8 x 7' (Supleco, Inc.)

6.6. An assortment of gas tight syringes from 0.1 ml to 1.0 liter volume - for standard preparation and sample injection (Hamilton Syringe or equivalent)

6.7. Pressure regulators for carrier gas, flame ionization detectors and standards - 2 stage, stainless steel diaphragm

6.8. Tedlar Bags in 1 or 3 liter sizes (SKC or equivalent).

6.9. Automated data systems capable of archiving instruments runs (Varian d-654, PE Nelson Turbochrom, or equivalent).

7. REAGENTS AND STANDARDS

7.1. High purity Helium for carrier gas, standard preparation, making dilutions, and purging blank water

7.2. Compressed Air for valve actuation

7.3. High purity Hydrogen for the Flame Ionization Detector

7.4. High purity Air for the Flame Ionization Detector

7.5. Prepared calibration standards. Standards are available at various concentrations commercially and are analytically certified by the supplier (Scott Specialty or equivalent).

7.6. Pure cylinders of Nitrogen, Carbon Dioxide, and Methane Room air can be used for the source of Oxygen/Argon, and also for Nitrogen at or below 78%.

7.7. Working standards. Standards are prepared at appropriate levels by making dilutions of the pure and prepared standards in Nitrogen using syringes and Tedlar Bags and/or pressure gauges in Summa or Silco canisters.

7.8. Reagent grade (distilled) water for blank preparation.

7.9. Reagent grade Hydrochloric Acid (1:1) for sample preservation (if required) and preserved blank preparation.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Water samples should be collected in the field or prepared in the lab by placing the water in a 40ml VOA vial. There should be no headspace present in the vial.

8.2. Add the water down the side of the bottle so as not to agitate or contaminate the sample. Fill to the top and cap using a Teflon-faced rubber septum and appropriate size crimp or screw-on cap. Care should be taken to eliminate or reduce the formation of bubbles.

8.3. Field samples should be fixed with 1:1 Hydrochloric Acid to a pH less than 2 before they are capped. Pre-preserved Voa vials may be used.

NOTE: DO NOT ADD ACID IF CARBON DIOXIDE IS TO BE DETERMINED, since it may convert inorganic carbon to carbon dioxide. The use of unpreserved Voa vials is recommended.

8.4. STL Los Angeles observes a holding-time of 14 days from the date of collection whether there is preservative added or not.

8.5. Samples must be stored at 4°C ± 2°C

9. QUALITY CONTROL

9.1. Initial Demonstration of Method Capability

9.1.1. Method Detection Limit (MDL) - A MDL must be determined prior to the analysis of any samples. The MDL is determined using seven replicates that have been spiked with the analyte of interest. These spiked replicates must be carried through the entire analytical procedure. MDL's must be determined and verified on an annual basis. The spike level must be between the calculated MDL and 10x the MDL to be valid. The result of the MDL determination must be below the reporting limit.

9.1.2. Demonstration of Capability (DOC) Study - Replicate LCS analysis. At the initiation of this method, four replicates of the LCS must be analyzed and evaluated to determine method accuracy and precision and the middle portion of the linear dynamic range. Results of the initial demonstration study must be acceptable before the analysis of samples may proceed. Annual DOC's are done to assure continued proficiency in the method for an analyst.

9.1.3. The department manager is responsible for ensuring that this procedure is performed by an analyst who has been properly trained and has the required experience.

9.2. Control Limits

9.2.1. When available, in-house historical control limits must be used for Laboratory Control Samples (LCS). These limits must be determined annually at a minimum. The recovery limits are determined as the mean recovery, ± 3 standard deviations for the LCS. Default limits are, at a minimum, 50% to 150% for recovery and 20% for the RPD between the LCS and the LCSD. In-house control limits may be tighter than the default limits.

9.3. Quality Control Batch

9.3.1. The QC batch is a set of up to 20 client samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain an LCS/LCSD pair and a method blank. Laboratory generated QC samples or instrument QC (MB, LCS/LCSD pair, calibration standards, ICV's and CCV's) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

9.4. Method Blanks

9.4.1. For each batch of up to 20 client samples, analyze a method blank consisting of Helium-purged reagent grade water with headspace prepared identically to the samples. The method blank is analyzed after the calibration standards, normally before any samples.

- Target analytes in the method blank must not exceed the reporting limit.

9.4.2. If there is no target analyte greater than the reporting limit (RL) in the samples associated with an unacceptable MB, the data may be reported with qualifiers. Such action should be done in consultation with the client and a NCM filed.

9.5. Laboratory Control Samples (LCS)

9.5.1. For each batch of samples, analyze an LCS/LCSD pair. The pair is analyzed after the calibration standard, and normally before any samples. The LCS contains all the analytes of interest in the mid-range of the calibration. If any analyte is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally include either the re-prep and/or reanalysis of the LCS, and sample reanalysis if there are samples that apply to the failed QC batch.

9.5.2. If the batch is not re-analyzed, the reasons for accepting the batch must be clearly presented in the project records, NCM and the report narrative.

- If reanalysis of the batch is not possible the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.
- If any analyte in the LCS exceeds the upper control limit and that analyte is not detected in the sample, then no corrective action is required. Document in an NCM.

10. CALIBRATION AND STANDARDIZATION

10.1. Standard Preparation

10.1.1. Standards are prepared in Tedlar Bags and/or Summa or Silco canisters using certified standards and static dilution techniques. Nitrogen is the diluent gas of choice.

10.2. Calibration and Verification

10.2.1. An initial calibration curve (ICAL) consisting of 5 points is run to determine the linear working range of the system for each compound. The low point should be at or below the reporting limit. A relative standard deviation (RSD) is calculated for each target analyte response factor using the calculation in Section 12. Each ICAL must have a %RSD less than 25% for each compound prior to analysis of samples.

10.2.2. Continuing Calibration Verification (CCV) standards for all target analytes are analyzed at a frequency of every 24 hours or 20 reportable continuously injected client samples, whichever is more frequent. Standards are prepared in Tedlar Bags using static dilution techniques and appropriate levels of gas standards certified by an outside supplier. Room air may be used for Nitrogen and Oxygen/Argon calibration. All target analyte RF's must be within 25%D of the initial calibration average RF's. Corrective action includes re-preparation and re-analysis of the standard, instrument maintenance and generation of a new initial calibration.

10.2.3. Once the above criteria have been met, sample analysis may begin. A closing CCV shall be injected if the sample batch cannot be finalized within the continuous injection period as defined above.

10.2.4. If sample analysis must be halted for more than an eight (8) hour period then an opening CCV must be analyzed to ensure that instrumentation conditions have remained stable.

10.2.4.1. If the opening CCV passes then sample analysis may proceed.

10.2.4.2. If the initial CCV fails, re-inject a second CCV. If the second CCV passes, analysis may proceed. If it fails, conduct maintenance and re-calibrate the instrument. Document the failure in the run log.

10.2.4.3. If the CCV's indicate valid instrument conditions, then the batch QC can be used for the data generated on two separate days.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and/or QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.1. Sample Analysis Procedure

11.1.1. GC parameters, nominal sample and QC volume, and sample temperature conditions are listed in Section 17.2.

11.1.2. All samples must be analyzed as part of a batch.

11.1.3. It is not necessary to reanalyze batch QC with reanalysis of samples. However, any reanalysis of samples must be associated with valid instrument QC.

11.1.4. Remove Voa's from refrigerator and allow to come to room temperature. Voa's should be at ambient temperature before they are extracted. Elevated sample temperatures are to be avoided, as they will affect sample results.

11.1.5. Fill a clean gas-tight syringe with a volume of contaminant-free Helium equal to 10% of the volume of the sample container. A standard 40ml VOA vial has been found to contain 43.5ml. Typically 4.4ml of sample is removed and replaced with Helium. Insert the needle of this syringe and another, empty gas-tight syringe through the septum of the sample container.

11.1.6. Slowly inject the Helium into the sample container while removing an equivalent volume of water with the other syringe.

11.1.7. Remove both syringes and agitate the bottle on a vortex for 5 minutes. **Caution: excessive handling of the sample should be avoided, as this will raise the temperature of the sample.**

11.1.7.1. If a vortex or automated shaker is not available, manual shaking can be used. The analyst must limit hand contact with the Voa, such as, only holding the ends of the vial with the fingertips.

11.1.8. After agitating the sample, use a 500µL gas-tight syringe to remove a 300µL aliquot of headspace sample. Inject the syringe's contents into the GC.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1. Retention time windows are set at +/- 0.5 minutes of the expected retention time as referenced to the CCV values. The reference method for RSK-175 does not address this issue.

12.2. Quantitative Analysis

12.2.1. The target analyte quantity is calculated by dividing the peak area of the target analyte by the average response factor of the ICAL, and applying any dilution factor generated, taking into account static dilutions and/or injection volumes.

12.2.2. The headspace concentration is calibrated and calculated as volume/volume (either %v/v or ppmv/v) and then used in the Henry's Law equation in section 12.4 to determine the concentration in water.

12.3. Calculations

12.3.1. The Turbochrom data system automatically quantitates the sample results based on a predetermined sample size. The results are in ppmv/v from the FID and %v/v from the TCD. The sample size is nominally 0.30 ml.

12.3.2. Calculation for Percent Relative Standard Deviation (%RSD):

%RSD = Std Dev of RF's/Mean of RF's X 100

12.3.3. Calculation for Percent Difference (%D):

% D = [(RF cpd CCV - ave. RF cpd ICAL)/ave. RF cpd ICAL]X 100

12.3.4. Calculation for Determining Concentration of Compounds in Headspace

Conc. Cpd = Area Cpd/ave. RF Cpd X DF

12.3.5. Calculation for Percent Recovery (%Rec):

% Rec = (Amount Cpd recovered/Amount Cpd Spiked) X 100

12.3.6. Calculation for Relative Percent Difference (RPD):

RPD= |Value A -Value B|/Average of Values X 100

12.3.7. Calculation of Decimal Fraction p_g

p_g = ppmv/v X 10^{-6} = %v/v X 10^{-2}

12.4. The following parameters are needed to perform Henry's Law calculations:

p_g = headspace concentration of analyte in decimal fraction, eg. 10ppm = 0.00001
H = Henry's Law Constant
ST = temperature of the sample (assumed to be standard temp. 298 °K)
bv = volume of sample bottle
hv = headspace volume

1) p_g = result in ppmv divided by 1000000 or result in %v/v divided by 100

2) equilibrium mole fraction of the dissolved gas, $x_g = p_g/H$

where H = Henry's Law Constant for the gas

3) Let n_g = moles analyte and n_w = moles water

Then $x_g = n_g / (n_g + n_w)$ and $n_g = x_g (n_g + n_w)$

If, $n_g * x_g << n_g$,

Then, $n_g = x_g * n_w$ or $n_g = n_w (p_g/H)$

Therefore; $n_g / V = n_w / V (p_g/H)$

4) One liter of water is 55.5 g-moles,

$n_g / V = 55.5 / L (p_g/H)$

5) Saturation concentration of the gas,

$C = (n_g/V) (MW) (1000 mg/g)$

where MW = molecular weight of the analyte

6) Density calculation

$p = (MW) / (22.4 l/mole) (ST in {}^{o}K /273 {}^{o}K)$

where: p = density
ST = sample temperature

7) $v = (bv_{mls} - hv_{mls}) (1L/1000mls)$

where: bv = bottle volume
hv = headspace volume

Then:

8) $A_h = hv_{mls} * p_g$

where A_h = ml of analyte in headspace

then liquid phase analyte (A_l) is

$A_l = (A_h/(v))(p_g)(1000 mg/g)(1L/1000ml)$

Then: $\underline{TC = A_l + C}$

Where: TC = Total Concentration of analyte in the original sample
A_l = liquid phase analyte
C = saturation concentration

The result will be in units of milligrams of gas per liter of water

12.5. Example Calculation:

p_g= 0.0018 (1800 ppmv/v) methane

Henry's Law Constant, H=4.13e4 for Methane

Sample Temperature 25 C (298 K)

Bottle Volume 60 ml

Headspace volume 6 ml

Using equation 2, x_g = 0.0018/4.13e4 or 4.358e-8 mole CH_4

Using equation 4 and the value above,

n_g/V = (55.5)(4.358e-8) or 2.42e-6 moles CH_4 per liter of water.

p = (16g/mole)/((22.4 l/mole)(298/273)) = 0.654 g CH_4 / liter H_2O

bv = 60 ml and hv = 6 ml, v = (60 ml - 6.0 ml)(1L/1000 ml) = 0.054 L

A_h = 6 ml, 0.0018 = 0.0108 ml CH_4

A_l = (0.0108 ml / 0.054 L)(0.654 g/L)(1L / 1000 ml) (1000 mg/g)

A_l = 0.1308 mg CH_4 / liter H_2O

Then TC = A_l + C = 0.038 mg/L + 0.131 mg/L = 0.169 mg / liter H_2O

13. REPORTING

13.1. Reporting Limits can be found in Section 18.5

13.2. Reporting Results

13.2.1. Estimates of uncertainty are based on historical control limits for the LCS. These limits can be provided when requested.

13.1. No conversion of the analytical results to the standard conditions is made.

14. METHOD PERFORMANCE

14.1. Method performance is controlled through the measurement of accuracy and precision. Analysis of a LCS and a LCSD are performed to measure both accuracy and precision. The control limits established for the LCS and LCSD are used to maintain method performance within a well-defined set of criteria.

15. WASTE MANAGEMENT AND POLLUTION PREVENTION

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by, and this method is set up in accordance with, section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention".

15.2. Waste Streams produced by this method.

15.2.1. Expired Standards – these are identified as expired, stored under manufacturer's recommended conditions and then lab packed for disposal.

15.2.2. Expired gas cylinders are emptied and returned to the manufacturer.

15.2.3. Sample Voa vials – maintained under refrigeration and then transferred to 55 gallon drums in the 90 day area.

16. REFERENCES

16.1. Newell, B.S., RSKSOP-175, Revision Number 0, August 1994, R.S. Kerr Environmental Research Laboratory of the United States Environmental Protection Agency.

16.2. Kampbell, D.H., J.T. Wilson, S.A. Vandegrift, Dissolved Oxygen and Methane in Water by GC Headspace Equilibration Technique, International Journal of Environmental Analytical Chemistry, Volume 36, pp. 249-257, 1991.

16.3. Vandegrift, S.A., RSKSOP-114, Revision Number 0, January 1991.

16.4. Newell, B.S., RSKSOP-147, Revision Number 0, August 1993.

16.5. Perry, J.H., *Chemical Engineer's Handbook*, (McGraw-Hill, NY, 1978), 5th ed.

16.5.1. Varian manual 3400 GC

16.5.2. PE Nelson Turbochrom manual

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Table 1 - Variables used in normal calculations

17.2. Table 2 - GC Conditions: Varian 3400

17.3. Table 3 - CCV and LCS Nominal Concentrations

17.4. Table 4 - Nominal ICAL Concentrations

17.5. Table 5 - Reporting Limits and Default Control Criteria

Table 1 - Variables used in normal calculations

Variable	Value	Units
Temperature	298	°K
Volume 40 ml VOA vial (bv)	43.5	ml
Volume headspace generated (hv)	4.4	ml
MW Methane	16	g/mole
MW Ethane	30	g/mole
MW Ethylene	28	g/mole
MW Carbon dioxide	44	g/mole
MW Oxygen	32	g/mole
MW Nitrogen	28	g/mole
MW Carbon Monoxide (25 deg C)	28	g/mole
Henry's Const. Methane (25 deg C)	4.13e+4	none
Henry's Const. Ethane (25 deg C)	3.02e+4	none
Henry's Const. Ethylene (25 deg C)	1.14e+4	none
Henry's Const. Carbon dioxide (25 deg C)	1.64e+3	none
Henry's Const. Oxygen (25 deg C)	4.38e+4	none
Henry's Const Nitrogen (25 deg C)	8.65e+4	none
Henry's Const. Carbon Monoxide (25 deg C)	5.80e+4	none

Table 2 - GC Conditions: Varian 3400

Initial Column Temp	65	Det B range (init)	12
Hold min	5.10	Det B autozero	yes
Prog 1 Temp	100	Det B range at time 0.01 min	11 no A/Z
Prog 1 rate deg/min	35	Det B range at time 5.0 min	12 no A/Z
Prog 1 hold min	11.9	A/S vial mode	off
Inj temp	100	Wait for ready	yes
Aux. Temp. (FID and reduction catalyst)	380	Initial Relays	-1-2-3-4
Detector temp (TCD)	150	Relays 0.01 min	+2
Det A range	0.50	Relays 2.85 min (may vary)	+3
Det A autozero	yes	Relays 8.00 min	-2
Det A filament temp	200	Relays 12.00 min	-3
Det A polarity positive	no	External Ox catalyst oven	550
Det A time program	no		

Table 3 - CCV and LCS Nominal Concentrations

Compound	CCV Concentration	LCS Concentration
Carbon Dioxide (TCD)	2.0 %v/v	1.0% v/v
Oxygen (TCD)	5.0% v/v	2.188 %v/v (10 % v/v air)
Nitrogen (TCD)	20.0% v/v	7.808 %v/v (10 % v/v air)
Methane (TCD)	2.0 %v/v	--
Carbon Dioxide (FID)	1,000 ppm v/v	10,000 ppm v/v
Ethylene (FID)	100 ppm v/v	500 ppm v/v
Ethane (FID)	100 ppm v/v	500 ppm v/v
Methane (FID)	100 ppm v/v	500 ppm v/v
Carbon Monoxide (FID)	100 ppm v/v	500 ppm v/v

Table 4 - Nominal ICAL Concentrations

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Carbon Dioxide (TCD) %v/v	0.10	0.50	1.0	2.0	10.0	50
Oxygen (TCD) %v/v	0.219	1.09	2.19	10.9	21.88	--
Nitrogen (TCD) %v/v	0.780	3.90	7.81	39.0	78.08	--
Methane (TCD) %v/v	0.10	0.50	1.0	5.0	10.0	50
Carbon Dioxide (FID) ppmv/v	100	500	1000	5000	10000	--
Ethylene (FID) ppm v/v	5	10	100	500	1000	--
Ethane (FID) ppm v/v	5	10	100	500	1000	--
Methane (FID) ppm v/v	10	100	500	1000	5000	10000
Carbon Monoxide (FID) ppm v/v	10	100	500	1000	5000	20000

Table 5 - Reporting Limits and Default Control Criteria

Compound	Reporting Limits	Control Limits % **	RPD %
Carbon Dioxide (TCD)	1.7 mg/l	50 - 150	20
Oxygen (TCD)	4.0 mg/l	50 – 150	20
Nitrogen (TCD)	10 mg/l	50 – 150	20
Methane (TCD)	0.10 mg/l	50 – 150	20
Carbon Dioxide (FID)	0.17 mg/l	50 – 150	20
Ethylene (FID)	0.0010 mg/l	50 – 150	20
Ethane (FID)	0.0020 mg/l	50 – 150	20
Methane (FID)	0.0010 mg/l	50 – 150	20
Carbon Monoxide (FID)	0.0010 mg/l	50 - 150	20

** Default limits, actual control limits may be tighter

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Implementation Date 1/24/03

STL North Canton
STANDARD OPERATING PROCEDURE

TITLE: TOTAL ORGANIC CARBON (TOC)

(SUPERSEDES: REVISION 2.1, DATED 08/17/00)

Prepared by:	Algiuta Colón	1/24/03 Date
Reviewed by:	Angela Serra — Technology Specialist	1/24/03 Date
Approved by:	Beth Lambert — Quality Assurance Manager	1/24/03 Date
Approved by:	Deborah S. Bucci — Environmental Health and Safety Coordinator	1/24/03 Date
Approved by:	[illegible] — Laboratory Director	1/24/03 Date

TABLE OF CONTENTS

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total Organic Carbon (TOC) in waters and similar matrices. It is based on SW846 Method 9060 and EPA Method 415.1. The working linear range is instrument dependent at 1 mg/L to 50 mg/L with a reporting limit of 1 mg/L.

1.2. QuantIMS method codes are DA (415.1) and FM (9060).

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. Organic Carbon is converted to carbon dioxide (CO_2) using chemical oxidation. The CO_2 is then measured by an infrared detector.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

4. INTERFERENCES

4.1. Contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts may cause Method interferences. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Carbonate and bicarbonate interfere but are eliminated by the acidification and purging step of the instrument.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the

Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive: Phosphoric Acid, Sulfuric Acid.**

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents {as well as glassware cleaning procedures that involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. O-I Corporation Model 1010 TOC Analyzer with 1051 vial multisampler and Printer

6.2. Nitrogen Gas and Regulator

6.3. Volumetric flasks: Various sizes

6.4. Volumetric pipettes: Various sizes

6.5. Vials: 40 mL glass

6.6. Graduated cylinders: Various sizes

6.7. pH Strips

6.8. Whatman filter #4

6.9. Top loading balance: capable of accurately weighing ± 0.01 g

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sodium Persulfate: Reagent Grade

7.1.2. Sodium Persulfate Solution: Add 200 g sodium persulfate ($Na_2S_2O_8$) to a 1 liter volumetric flask and dilute to volume with reagent water.

7.1.3. Phosphoric Acid, concentrated: Reagent Grade

7.1.4. Phosphoric Acid Solution: Carefully add 59 mL concentrated phosphoric acid (H_2PO_4) to 900 mL of reagent water in a 1 liter volumetric flask. Dilute to volume with reagent water.

7.1.5. Sulfuric Acid, concentrated: Reagent Grade

7.2 Standards

7.2.1. All standards should be prepared in volumetric flasks, using volumetric pipettes, and diluted to volume with reagent water.

7.2.2. TOC Stock Standard

7.2.3. Primary and secondary sources are needed.

7.2.3.1.TOC 1000 mg/L

7.2.3.1.1. Dilute 1.06 g KHP (potassium acid phthalate) to volume in a 500 mL volumetric flask. A commercially prepared solution may also be used.

7.2.3.2.Prepare every six months.

7.2.4. TOC Calibration Standards

7.2.5. Prepare the following standards from the primary stock standard described in Section 7.2.2.2.1.

Concentration (mg/L)	Volume (mL)	Stock Concentration (mg/L)	Final Volume (mL)
50	5	1000	100
25 (MS/MSD) (LCS)	12.5	1000	500
10	1	1000	100
1	0.1	1000	100

7.2.6. TOC Verification Standard (LCS)

7.2.6.1. A commercially prepared solution is used.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples are preserved to a pH <2 with sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) and stored in plastic or glass containers at 4°C±2°C.

8.2 The holding time is twenty-eight days from sampling to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including

preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A method blank consisting of 40 mL of reagent water and all reagents added to the samples must be prepared and analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be taken in consultation with the client and must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. Laboratory Control Samples are well characterized; laboratory generated samples used to monitor the laboratory's day to day performance of routine analytical methods. The LCS is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.3.2. A purchased LCS must be analyzed with each batch of samples.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.3. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. An MS/MSD consisting of 20 mL of sample and 20 mL of the 25 mg/L standard will be analyzed with each analytical batch of samples.

9.4.3. Corrective action for MS/MSDs

9.4.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.3.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page "NC The recovery and/or RPD were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."

9.4.3.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.5. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021.

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Recommended Initial Setup

Contant Settings		
STD Mass	=	6.76 ug C
Sample Vol	=	2.0 mL
Acid Vol	=	4 x 100 uL
Oxidant Vol	=	10 x 100 uL

10.1.1 Adjust the nitrogen to 30 psi using the flow valve on the tank. The gauge should always be set at 30 psi when the instrument is not in use.

10.1.2 Remove the reagent bottles and fill with appropriate reagents (phosphoric acid solution and sodium persulfate). Do not fill bottles completely full; leave a small amount of air space. Loosely reconnect caps (and tubing), and replace the bottles into the instrument.

10.1.3 Blank and calibrate the instrument when CCVs and/or CCBs fail to meet acceptance criteria or when other problems are encountered.

10.1.3.1. Choose "Calibration". Start a new file with the current date.

10.1.3.2. Choose "Sequences" from the "databases" menu option, open up the calibration template.

10.1.3.3. Confirm all information. If blanking is required, it is best if done before calibration. Enter the desired number of blanks (no less than five) in the "reagent blanks before" field.

10.1.3.4. Analyze an ICV/ICB

10.1.3.5. Save the file using the current date as the filename.

10.1.3.6. Update data file information.

10.1.3.6.1. Choose the setup menu option, go into win TOC output, change the log fill name and prefix counter.

10.1.3.7. When analysis is complete, print the run from "/utilities/view run log"

10.1.3.8. Evaluate the data. The correlation coefficient of the original curve must be =0.995 or recalibration is required.

10.2. Continuing Calibration

10.6.1. The run is checked at the beginning, after every ten samples, and at the end of the run of the same species using a midrange CCV made from a primary source (Section 7.2.4. or 7.2.7.) to verify continued linearity. A CCV cannot vary from the original curve by more than ± 10%, or recalibration is required.

10.6.2. System cleanliness is checked every ten samples and at the end of the run using Continuing Calibration Blank (CCB). A CCB cannot contain the analyte of interest above the reporting limit, or recalibration is required.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Sample Preparation Procedure

11.2.1. If excess particulate matter exists, filter an aliquot of sample through a Whatman #4 filter into a TOC vial or decant.

11.3. Preparation Documentation

11.3.1. Record any sample preparation on the analytical logsheet.

11.4. Analytical Documentation

11.4.1 Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.4.2 All standards are logged into a department standard logbook. All standards are assigned a unique number for identification. The supervisor or designee reviews logbooks.

11.4.3 Documentation, such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs, is available for each data file.

11.4.4 Sample results and associated QC are entered into the Laboratory Information Management System (LIMS) after final technical review.

11.4.5 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12 DATA ANALYSIS AND CALCULATIONS

12.1. Sample Analysis Procedure

12.1.1. Type a run protocol sequence into the computer using the run template, if desired. Update the data file information in the setup/win TOC output.

12.1.2. For method 9060, quadruplicate analysis is required. If quadruplicate reporting is requested, each of four results are reported. Replicate analysis should be taken from separate vials, if available. If only one reportable result is requested per sample, the four results should be taken from one vial, and the average of the four results are reported.

12.1.3. For method 415.1 only one analysis is required. The single analysis is reported directly from the instrument printout.

12.1.4. All samples and standards should be poured into 40 mL vials. Samples received in vials can be run in those containers, provided there is not an excess of solids.

12.1.5. Be sure the samples are loaded on the sampler, the first one positioned under the needle.

12.1.6. Click the "Start" button.

12.1.7. Samples that fall outside the linear range (>50 mg/L) of the instrument must be diluted and reanalyzed.

12.1.7.1. Samples following a high sample should be re-analyzed if carryover is a concern.

12.1.8. Print the run from "utilities/view run log".

12.1.9. When analysis is complete, properly dispose of or put away samples and standards.

12.2. Calculations for 9060 only

12.2.1. Total Organic Carbon, mg/L = Average Instrument Value x Dilution

Where:

TOC, mg/L = average of the 4 instrument values x dilution, calculated (without dilution) by the instrument.*

12.2.2. $$LCS\ \%\ Recovery = \frac{\textit{Iinstrument values*}}{\textit{True Value}} \times 100$$

12.2.3. MS/MSD % recovery

$$\left(\frac{(Iinstrument\ values * MS\ or\ MSD) - (Avg\ sample\ instrument\ value * \div 2)}{12.5}\right) x100$$

**One of the values may be judged erroneous and disregarded if three of the four are consistent. If no consistency can be found in the four values, the sample must be rerun.*

13 METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Acid waste must be collected in clearly labeled acid waste containers.

15.2. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan.

15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

15.5. Solvent waste must be disposed of in clearly labeled waste cans.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Total Organic Carbon, Method 9060.

16.1.2. EPA 600, Methods for Chemical Analysis of Water and Wastes, Organic Carbon, Method 415.1.

16.1.3. Corporate Quality Management Plan (QMP), current version.

16.1.4. STL Laboratory Quality Manual Plan (LQMP), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit is 1 mg/L

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Troubleshooting guide

17.2.1. See the manufacturer's instructions for an instrument troubleshooting guide and maintenance requirements.

17.3. Method deviations

17.3.1. A blender is not used to homogenize samples.

17.3.2. For Method 9060, the calibration must be verified with an independently prepared check standard every 15 samples. The laboratory is verifying the calibration every 10 samples.

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Implementation Date: 4/10/01

SOP No. NC-WC-0018
Revision No. 2.1
Revision Date: 03/30/01
Page 1 of 12

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: TOTAL ORGANIC CARBON (TOC) ANALYSIS FOR NON-WATERS

(SUPERSEDES: REVISION 2.0 DATED 02/27/97)

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Date

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Approved by: Christopher McQuade 4-9-01
Laboratory Director Date

Proprietary Information Statement:

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TABLE OF CONTENTS

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total Organic Carbon in liquid, oils, sludge, soil, and sediment samples. It is based on Methods of Soil Analysis, Walkley-Black. The working linear range is 100 to 15,000 mg/kg.

1.2. The associated QuantIMs method code is VR.

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

2. SUMMARY OF METHOD

2.1. An aliquot of a solid sample is treated with excess potassium dichromate and concentrated sulfuric acid. After treatment, the solution is backtitrated with ferrous sulfate to determine the amount of dichromate reduced during digestion.

3. DEFINITIONS

3.1. Refer to the glossary in the STL Laboratory Quality Manual (LQM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Chloride and iron give a positive interference. Chloride may be totally or partially eliminated by the addition of mercuric sulfate.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazard is known:

5.3.1. The following material is known to be **corrosive: Sulfuric acid**.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents {as well as glassware cleaning procedures that involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Buret: 25 mL Class A

6.2. Analytical balance: capable of weighing to ± 0.0001 g

6.3. Top loading balance: capable of weighing to ± 0.01 g

6.4. Amber bottles

6.5. Beakers: various

6.6. Graduated cylinders: various

6.7. Volumetric pipettes: various , Class A

6.8. Erlenmeyer flasks: various

6.9. Whatman #4 filter paper

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sulfuric Acid ($H_2 SO_4$): concentrated, Tracepur grade

7.1.2. Ferroin indicator, purchased

7.1.3. Potassium Dichromate ($K_2Cr_2O_7$): primary standard grade

7.1.4. 1N Potassium Dichromate Solution: Accurately weigh 49.04 g of potassium dichromate (dried overnight at 105°C) in a liter volumetric flask and dilute to volume. Store in amber bottle and refrigerate. Replace after six months.

7.1.5. Ferrous Sulfate ($FeSO_4 \bullet 7 H_2O$): reagent grade

7.1.6. 0.5 N Ferrous Sulfate Titrant: Accurately weigh 140 g of $FeSO_4 \bullet 7H_2O$ into a 1 liter volumetric flask and dissolve with 500 mL reagent water. Carefully add 15 mL of concentrated sulfuric acid and allow to cool. Dilute to volume with reagent water. Store in amber bottle and refrigerate.

7.1.7. Mercuric Sulfate ($HgSO_4$): reagent grade

7.2. Standards

7.2.1. Laboratory Control Sample

7.2.1.1.Potassium Hydrogen Phthalate ($KHC_8H_4O_4$), purchased

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are stored in a glass container at 4°C ± 2°C.

8.2. Samples are not chemically preserved. In lieu of no guidance, holding time is based on water requirements.

8.3. The holding time is twenty-eight days from sampling to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A reagent water blank consisting of 200-mL reagent water is being prepared and analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A midrange LCS using 0.02 g of potassium hydrogen phthalate is prepared and analyzed with each batch of samples.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.3. Corrective action will be reprepparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Sample Duplicate

9.4.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.4.2. Sample duplicates are performed at a frequency of 10% or one per batch which ever is more frequent and must meet laboratory-specific limits for precision.

9.5. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual

(LQM) and the latest is version easily accessible via the LIMs (QC Browser program).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021.

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. The ferrous sulfate titrant is standardized daily as follows.

10.1.1. Pipette 10.0 mL of 1.00 N potassium dichromate solution into a 250 mL Erlenmeyer flask and add 90-mL reagent water.

10.1.2. Carefully add 30 mL of concentrated sulfuric acid and allow cooling completely.

10.1.3. Add 2-3 drops of ferroin indicator.

10.1.4. Titrate with 0.5 N ferrous sulfate titrant to a reddish-brown endpoint or to the first color change after reaching an emerald-green color.

10.1.5. Calculate the normality using the following equation.

$$N = \frac{10}{mL\ ferrous\ sulfate}$$

10.1.6. Repeat steps 10.1.1 through 10.1.5 two more times.

10.1.7. The average of the triplicate standardization is used.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Physical Preparation

11.3.1.1. Mix the sample thoroughly before selecting a portion for analysis.

11.3.1.2. Discard any foreign objects such as sticks, leaves, and rocks.

11.3.2. Analytical Preparation

11.3.2.1. Weigh an aliquot of soil of 2.50 g to the nearest 0.01 g (use less sample if TOC is known to be high). Record the weight on the analytical logsheet.

11.3.2.2. Place sample in a 500 mL Erlenmeyer flask and add 10.0 mL of 1 N potassium dichromate.

11.3.2.3. Under a hood, carefully add 20 mL of concentrated sulfuric acid and gently swirl for one minute.

11.3.2.4. Allow sample to cool for about 30 minutes.

11.3.2.5. Add 200 mL of reagent water and swirl to mix. If necessary, filter sample through Whatman #4 filter.

11.4. Sample Analysis Procedure

11.4.1. Add 2-3 drops ferroin indicator.

11.4.2. Titrate with 0.5 N ferrous Sulfate Solution to a reddish-brown endpoint or first color change after reaching an emerald-green color.

11.4.2.1. If the digestate of the sample is already green or reddish-brown after the addition of the ferroin indicator, the sample needs to be re-extracted with a smaller sample amount or if less than 5 mLs of titrant is used.

11.4.3. Document the amount of titrant on the analytical logsheet.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2. All standards are logged into a department standard logbook. All standards are assigned a unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. **Total Organic Carbon, mg/kg =**

$$\left[\frac{\textbf{[(10)(N Potassium Dichromate) - (mL Ferrous Sulfate) (N Ferrous Sulfate)]}}{\textbf{Weight of Soil (g)}} \textbf{ x 3000}\right] \times \textbf{ 1.3}$$

Where: *1.3 = Correction factor recommended in method*

12.2. $$\textbf{TOC, \%} = \frac{\textbf{mg / kg}}{\textbf{10,000}}$$

12.3. $$\textbf{LCS, \%} = \frac{\textbf{TOC, \%}}{\textbf{61.152 (true)}} \textbf{ x 100}$$

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Solvent waste must be disposed of in clearly labeled waste cans.

15.2. Acid waste must be collected in clearly labeled acid waste containers.

15.3. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4. Refer to the Laboratory Sample and Waste Disposal plan.

15.5. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. Methods of Soil Analysis, 1982 Second Edition Method 29-3.5.2 Walkley-Black Procedure.

16.1.2. STL North Canton Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) for undiluted samples is 100 mg/kg.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Troubleshooting guide

17.2.1. When interferences as described in Section 4 are encountered or suspected, treat the sample as specified in that section.

17.2.2. If a high level of TOC is suspect (black sample), a smaller amount will be required.

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Implementation Date: 10/16/00

SOP No: NC-WC-0084
Revision No: 3
Revision Date: 10/03/00
Page 1 of 22

STL STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

(SUPERSEDES: REVISION (2))

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Date

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Approved by: [signature] 10/11/00
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1. SCOPE AND APPLICATION

1.1. This method covers the determination of fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate and sulfate in drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 11.7) and leachates (when no acetic acid is used).

1.2. A listing of associated LIMs method codes is located in Section 8.2.

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. A 25 uL volume of sample is introduced into the ion chromatograph. The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a precolumn or guard column and a separator column, are packed with low-capacity, strongly basic anion exchange resin. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppresser column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM).

4. INTERFERENCES

4.1. Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2. The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of concentrated eluent to each standard and sample.

4.3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or an elevated baseline in the ion chromatograms.

4.4. Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.5. The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfied ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore; unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation when possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2. Ion Chromatograph -- Analytical system complete with ion chromatograph and all required accessories including analytical columns, compressed gases and detectors.

6.2.1. Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with same substrate as the separator column. 4 x 50 mm, Dionex IonPac AG14 P/N 46134, or equivalent.

6.2.2. Anion separator column: The separation shown in Figure 1 was generated using a Dionex IonPac AS14 column (P/N 46134). Equivalent column may be used if comparable resolution is obtained, and the requirements of Sect. 9.2 can be met.

6.2.3. Anion suppresser device: Dionex anion micro membrane suppresser (P/N 37106) or ASRS-Ultra Self-Regenerating Suppressor (4mm) P/N 53946 or equivalent.

6.2.4. Detector – Conductivity cell: approximately 1.25 uL internal volume, Dionex, or equivalent.

6.2.5. Dionex –PeakNet 5.1Data Chromatography Software or equivalent.

6.3. Assorted laboratory glassware (pipettes, volumetric flasks, etc.).

7. REAGENTS AND STANDARDS

7.1. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2. Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.3. Eluent solution: sodium bicarbonate (CASRN 144-55-8) 1.0 mM, sodium carbonate (CASRN 497-19-8) 3.5 mM. Dissolve 1.680 g sodium bicarbonate ($NaHCO_3$) and 7.417 g

of sodium carbonate (Na_2CO_3) in reagent water (7.2) and dilute to 100 mL in a volumetric flask. Take 10 mL of this concentrated eluent solution and dilute to 2 L for use as the working eluent solution or dissolve the entire bicarbonate/carbonate amount in 20 L of reagent water.

7.4. Stock solutions (1,000 mg/L): All stocks may be prepared as described below or purchased from commercial sources. Primary and secondary sources are required for each target analyte.

7.4.1. Fluoride stock solution (1.00 mL = 1.00 mg F^-): In a 1 liter volumetric flask, dissolve 2.2100 g of sodium fluoride (NaF) in reagent water, and dilute to volume with reagent water. Store in chemical- resistant glass or polyethylene.

7.4.2. Chloride stock solution (1.00 mL = 1.00 mg Cl): Dry sodium chloride (NaCl) for 12 hours at 105°C, and cool in a desiccator. In a 1 liter volumetric flask, dissolve 1.6485 g of the dry salt in reagent water and dilute to volume with reagent water.

7.4.3. Nitrite stock solution (1.00 mL = 1.00 mg NO_2^- - N): Place approximately 10.0 g of sodium nitrite (KNO_2) in a 125 mL beaker and dry to constant weight (about 24 hours) in a desiccator. In a 1 liter volumetric flask, dissolve 6.0790 g of the dried salt in reagent water and dilute to volume with reagent water. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

- Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.
- Prepare sterile bottles for storing nitrite solutions by heating for 1 hour at 170°C in an air oven.

7.4.4. Bromide stock solution (1.00 mL = 1.00 mg Br^-): Dry approximately 5.0 g of sodium bromide (NaBr) for 12 hours at 105°C, and cool in a desiccator. In a 1 liter volumetric flask, dissolve 1.2876 g of the dried salt in reagent water and dilute to volume with reagent water.

7.4.5. Nitrate stock solution (1.00 mL = 1.00 mg NO_3^- - N): Dry approximately 10.00 g of sodium nitrate (KNO_3) at 105°C for 24 hours . In a 1 liter volumetric flask, dissolve 7.2200 g of the dried salt in reagent water and dilute to volume with reagent water.

7.4.6. Phosphate stock solution (1.00 mL = 1.00 mg PO_4 - P): Dry approximately 10.00 g of potassium dihydrogen phosphate (KH_2PO_4) for 1 hour at 105°C and cool in a

desiccator. In a 1 liter volumetric flask, dissolve 4.3937 g of the dry salt in reagent water and dilute to volume with reagent water.

7.4.7. Sulfate stock solution (1.00 mL = 1.00 mg SO_4^{-2}): Dry approximately 5.00 g of potassium sulfate (K_2SO_4) at 105°C for 1 hour and cool in a desiccator. In a 1 liter volumetric flask, dissolve 1.8141 g of the dried salt in reagent water and dilute to volume with reagent water.

7.4.8. Commercial stock solution A: F^- - 25 mg/L, Cl^- - 500 mg/L, Br^-- 100 mg/L, NO_3^- - N- 25 mg/L, PO_4 – P - 25 mg/L, SO_4^{-2}- 500 mg/L

7.4.9. Commercial stock solution B: NO_2^- - N- 25 mg/L

7.4.10. Commercial IC Spike solution A: : F^- - 125 mg/L, Cl^- - 2500 mg/L, Br^-- 500 mg/L, NO_3^- - N- 125 mg/L, PO_4 – P - 125 mg/L, SO_4^{-2}- 2500 mg/L

7.4.11. Commercial IC Spike solution B: NO_2^- - N- 125 mg/L

7.5. Working standards: Prepare calibration standard #5 in a 10 mL volumetric flask and transfer to a vial. Adjust the amount of stock solution used to prepare the working standards if the stock concentration differs from 1000 mg/L as assumed Alternatively prepare Cal standard #5 by mixing 4.0 mL commercial stock A, 4.0 mL commercial stock B and 2.0 mL of reagent water.

Calibration Standard #5

Analyte	mL of Stock	Final Conc.
Fluoride	0.10mL	10.0 mg/L
Chloride	2.0 mL	200. mg/L
Nitrite	0.10 mL	10.0 mg/L
Bromide	0.40 mL	40.0 mg/L
Nitrate	0.10 mL	10.0 mg/L
Ortho-Phosphate	0.10 mL	10.0 mg/L
Sulfate	2.0 mL	200. mg/L

7.5.1. In 5 mL PolyVials prepare the following calibration standards in reagent grade water. Final concentrations of working standards are shown below.

Calibration Standard #4: take 2.50 mL of calibration standard #5 and add 2.50 mL of reagent water.

Calibration Standard #2: take 250 µL of calibration standard #5 and add 4.75 mL of reagent water.

Calibration Standard #1: take 25.0 µL of calibration standard #5 and add 4.95 mL of reagent water.

Calibration Standard #3: take 1 25 mL of calibration standard #5 and add 3.75 mL of reagent water.

Calibration Standard #1

Analyte	25.0 µL of Cal Std #5	Final Conc
Fluoride		0.05 mg/L
Chloride		1.0 mg/L
Nitrite		0.05 mg/L
Bromide		0.20 mg/L
Nitrate		0.05 mg/L
Ortho-Phosphate		0.05 mg/L
Sulfate		1.0 mg/L

Calibration Standard #2

Analyte	250 µL of Cal Std #5	Final Conc.
Fluoride		0.5 mg/L
Chloride		10. mg/L
Nitrite		0.5 mg/L
Bromide		2.0 mg/L
Nitrate		0.5 mg/L
Ortho-Phosphate		0.5 mg/L
Sulfate		10. mg/L

Calibration Standard #3

Analyte	1.25 mL of Cal Std #5	Final Conc.
Fluoride		2.5 mg/L
Chloride		50. mg/L
Nitrite		2.5 mg/L
Bromide		10. mg/L
Nitrate		2.5 mg/L
Ortho-Phosphate		2.5 mg/L
Sulfate		50. mg/L

Calibration Standard #4

Analyte	2.5 mL of Cal Std #5	Final Conc.
Fluoride		5.0 mg/L
Chloride		100 mg/L
Nitrite		5.0 mg/L
Bromide		40. mg/L
Nitrate		5.0 mg/L
Ortho-Phosphate		5.0 mg/L
Sulfate		100 mg/L

7.5.2. Prepare or purchase a secondary stock standard(s) using a standards source other than that used for the primary standards as described in Section 7.5. Dilute these stock standards to as indicated in the table below to prepare the mixture to be used for the LCS and CCV solution. Alternatively prepare this solution by mixing 0.50 mL commercial stock A, 0.50 mL commercial stock B and 4.0 mL of reagent water.

LCS & Continuing Calibration Verification Solution

Analyte	Final Conc. (V_f=5ml)
Fluoride	2.5 mg/L
Chloride	50. mg/L
Nitrite	2.5 mg/L
Bromide	10. mg/L
Nitrate	2.5 mg/L
Ortho Phosphate	2.5 mg/L
Sulfate	50. mg/L

7.5.3. Prepare or purchase a secondary stock standard(s) using a standards source other than that used for the primary standards as described in Section 7.5. Dilute these stock standards to prepare the mixture to be used for the Matrix Spike solution. Alternatively purchase these mixes (ready to use) from a commercial source. Add 100 uL of each IC Spike solution to 5 mL of sample when preparing the MS/MSD. Dilute as needed after spiking the sample.

Matrix Spike "True" Values

Analyte	Final Conc.
Fluoride	2.5 mg/L
Chloride	50. mg/L
Nitrite	2.5 mg/L
Bromide	10. mg/L
Nitrate	2.5 mg/L
Ortho Phosphate	2.5 mg/L
Sulfate	50. mg/L

NOTE: Stock standards, calibration standard #5 and LCS standard should be stored in the dark at 4° ± 2°C. Replace these standards when instrument response indicates target analyte

degradation may have occurred or after the standard has expired (12 months commercial mix or 6 months in house mix), which ever occurs first. Nitrite and ortho-phosphate are particularly light and oxygen sensitive.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

8.2. Sample preservation and holding times for the anions that can be determined by this method for water samples are as follows:

QuanTIMs Method Code		Analyte	Preservation	Holding Time
EPA 300.0A	SW846 9056A	Fluoride	4° ± 2°C	28 days
C8	3C			
CX	3D	Chloride	4° ± 2°C	28 days
GO	3E	Nitrite	4° ± 2°C	48 hours
GM	3F	Bromide	4° ± 2°C	28 days
C9	3G	Nitrate	4° ± 2°C	48 hours
DO	3H	Ortho Phosphate	4° ± 2°C	48 hours
CY	3I	Sulfate	4° ± 2°C	28 days

Note: Soil leachates will follow the same preservation and holding times as the water samples; starting from the time of extraction.

9. QUALITY CONTROL

9.1. The STL QC Program document provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required.

9.2. Table I provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.3. Initial Demonstration of Capability

9.3.1. Prior to the analysis of any samples by Ion Chromatography, the following requirements must be meet:

9.3.1.1. Method Detection Limit (MDL): An MDL must be determined prior to analysis of any samples. The MDL is determined using seven replicates of reagent water spiked with the anions of interest that has been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis. The spike level must be greater than the calculated MDL but less than or equal to 10x the MDL. The result of the MDL determination must be below the STL reporting limit.

9.4. Batch definition: Preparation and QC batch definitions are provided in the STL QC Policy.

9.5. Method Blank (MB): One method blank must be processed with each preparation batch. The method blank consists of reagent grade water that has been taken through the entire preparation and analytical process. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest above the reporting limit.

9.6. Laboratory Control Sample (LCS): One LCS must be processed with each preparation batch and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. If the result is outside established control limits the system is out of control and corrective action must occur. Until in-house limits are established, a control limit of 90 - 110% recovery must be applied. Corrective action will be reprepparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable. The LCS consists of reagent grade water containing a known amount of target analytes that has been injected into the ion chromatography system. The LCS is prepared from a separate stock standard, or neat material, of a different manufacturer than the stock, or neat material, used to prepare the calibration standard.

9.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD): One MS/MSD pair must be processed for each QC batch. A matrix spike (MS) is a field sample to which a known concentration of target analyte has been added. A matrix spike duplicate (MSD) is a second aliquot of the

same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific DQO's may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Spiking levels will be the same as the LCS values.

- If the MS/MSD recovery or RPD falls outside the acceptance range, the recovery of the analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 90-110% recovery and 20% RPD must be applied to the MS/MSD.
- If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data are reported as NC (i.e. not calculated).
- If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.
- If the recovery of the LCS is outside the limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.
- If a MS/MSD is not possible due to limited sample volume then a LCS duplicate must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike limits.

9.8. Continuing Calibration Verification (CCV/CCB): Continuing calibration is verified by analyzing the calibration standard after every ten (10) samples . The CCV must fall within +/- 10% of the true value for each target analyte. A CCB is analyzed immediately following the CCV to monitor low level accuracy and system cleanliness. The CCB result must be below the reporting limit for that analyte. If either the CCV or CCB fail to meet criteria, the analysis must be terminated, the problem corrected and repreparation and analysis of all samples following the last CCV and CCB which were in control.

10. CALIBRATION AND STANDARDIZATION

10.1. Establish ion chromatographic operating parameters equivalent to those indicated in table 2. Refer to Table 3 for typical standard run retention times. Other than the presence of the analytical column the instrument conditions are the same.

10.2. For each analyte of interest, prepare a **minimum** of 3 calibration standards and a blank by adding accurately measured volumes of one or more stock standards to a volumetric flask and dilution to volume with reagent water. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

10.3. Using an injection volume of 25 uL of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded. All analytes will be calibrated using a quadratic regression forced through the origin. Correlation coefficients (R^2) must be 0.995 or better.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Table 2 summarizes the recommended operating conditions for the ion chromatograph. Included in this table are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 9.2 are met.

11.4. Check system calibration daily as outlined in Table 1 and, if required, recalibrate as described in Sect 10.

11.5. Load and inject a fixed amount (25 uL) of settled & filtered sample. If the sample is cloudy then it should be filtered prior to loading into the autosampler polyvial. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.6. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of various concentration. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte.

However, the experience of the analyst should weigh heavily in the interpretation of chromatograms since retention time is concentration dependent for most analytes..

11.7. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.8. If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

NOTE: Retention time is affected by concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. See Table 3. In some cases this peak migration may produce poor resolution or identification.

11.9. The following extraction should be used for solid materials: Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed for one hour using a magnetic stirring device or tumbler. Filter the resulting slurry before injecting using a 0.45 um membrane type filter. This can be the type that attaches directly to the end of the syringe

11.10. Should more complete resolution be needed between peaks the eluent (7.3) can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Prepare a calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

12.2. Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3. Report results in mg/L for aqueous samples and mg/Kg for 1 hour leachates and mg/L for 18 hour leachates of solid samples.

12.4. Report NO_2^- as N

NO_3^- as N

$HPO_4^=$ as P

13. METHOD PERFORMANCE

13.1. The reporting limits for the following analytes are based on a 25 uL injection volume:

Analyte	Water RL	Soil RL
Fluoride	1.0 mg/L	10 mg/kg
Chloride	1.0 mg/L	10 mg/kg
Nitrite	0.5 mg/L	5 mg/kg
Bromide	0.5 mg/L	5 mg/kg
Nitrate	0.05 mg/L	0.5 mg/kg
O-Phosphate	0.5 mg/L	5 mg/kg
Sulfate	1.0 mg/L	10 mg/kg

13.2. The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. The analyst must be given two blind performance samples to analyze or process for analysis. Upon successful completion of the performance evaluation (PE) samples, these analyses will be documented as initial qualification,. Requalification must be performed annually thereafter for this procedure. The group/team leader must document the training and PE performance and submit the results to the QA Manager for inclusion in the associate's training files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure must be segregated, and disposed of according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Method 300.0, "Determination of Inorganic Anions by Ion Chromatography", Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio, Revision 2.1, August 1993.

16.2. Method 9056A, "Determination of Inorganic Anions by Ion Chromatography", SW846, Test Methods for Evaluating Solid Waste, Third Edition, Draft Revision 1, September 1999.

16.3. STL North Canton Laboratory Quality Manual (LQM), current version.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Attachment #1, method Flow Chart

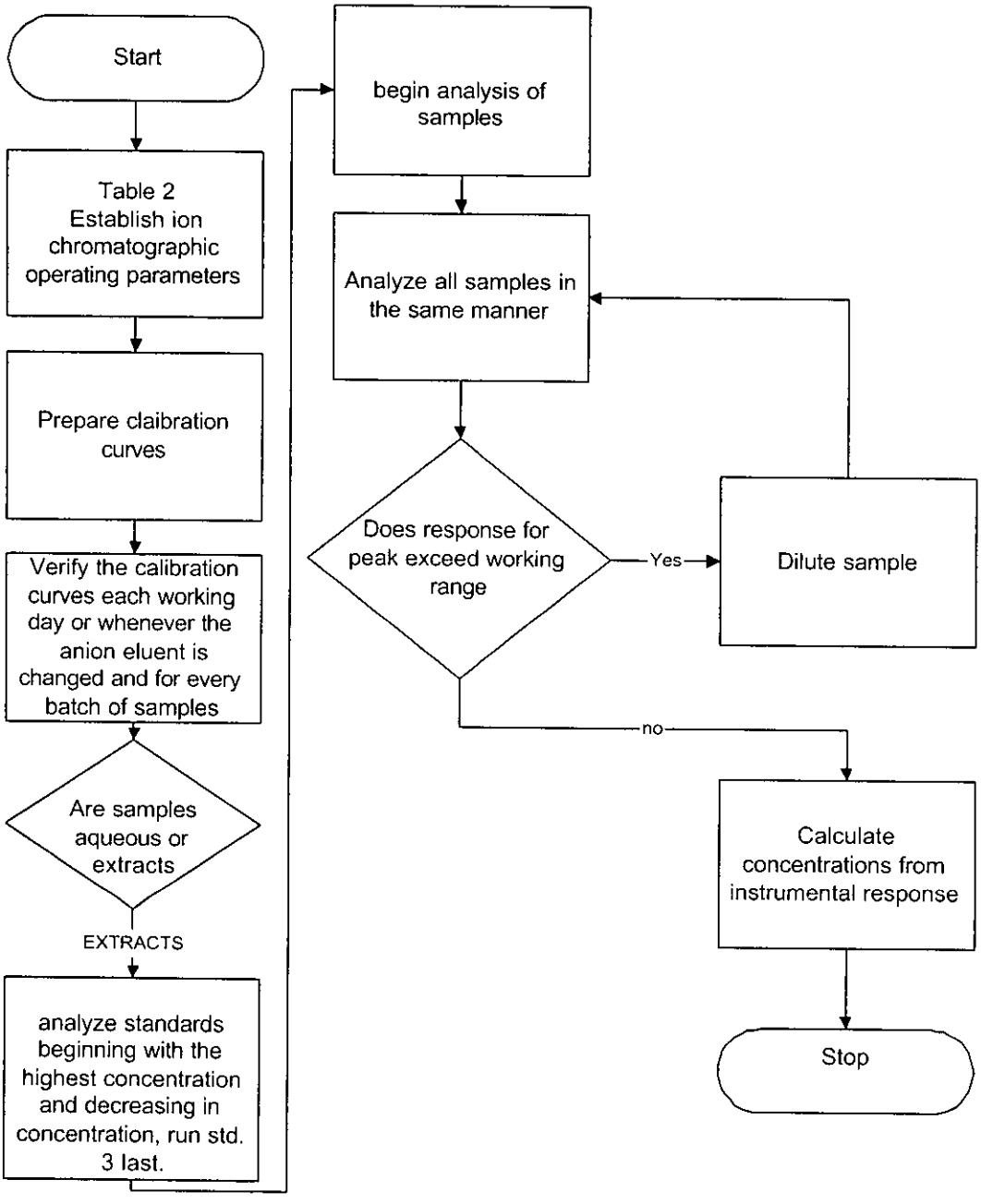
17.2. Table 1, Quality Control Samples

17.3. Table 2, Standard Instrument Operating Parameters

17.4. Table 3, Retention Time Matrix

17.5. Figure 1, Example Chromatogram

Determination Of Inorganic Anions By Ion Chromatography



ATTACHMENT #1

TABLE 1

QUALITY CONTROL SAMPLES

QC Samples	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Verification (ICV)	At the start of each day following calibrating prior to sample analysis	+/- 10% of true value	Recalibrate and reanalyze
Initial Calibration Blank (ICB)	After Initial Calibration Verification and prior to sample analysis	< the Reporting Limit	Reprepare and reanalyze
Laboratory Control Sample (LCS)	1 per batch of 20 samples	Meets laboratory historical limits	Reanalyze all samples associated with unacceptable LCS
Matrix Spike Sample (MS/MSD)	1 MS/MSD pair per batch or 20 samples	Meets laboratory historical limits	Supervisor's technical judgment
Continuing Calibration Verification (CCV)	Between each group of 10 injections and at the end of the analytical sequence	+/- 10% of true value	Recalibrate and reanalyze all samples since the last acceptable CCV
Continuing Calibration Blank (CCB)	Between each group of 10 injections and at the end of the analytical sequence	< the Reporting Limit	Recalibrate and reanalyze all samples since the last acceptable CCB

TABLE 2

Standard Instrument Operating Parameters

Standard Conditions:

Eluent Pump Rate:	1.20 mL/min (DX-120 and DX-320)
Sample Loop:	25 uL
Eluent:	1.0mM sodium bicarbonate, 3.5mM sodium carbonate
Detector output	Baseline conductivity should be 15 - 20 uS prior to sample analysis.

TABLE 3

Standard Run Retention Time Matrix (minutes)*

	Concentration (mg/L)													
Analyte	0.05	0.2	0.5	1	2	2.5	5	10	20	40	50	100	200	RT window
F^-	2.75		2.75			2.75	2.75	2.75						
Cl^-				3.97				3.98			4.03	4.08	4.17	
NO_2^-	4.80		4.80			4.78	4.78	4.80						
Br^-		6.15			6.13			6.10	6.08	6.07				
NO_3^-	7.33		7.27			7.17	7.13	7.07						
$o\text{-}PO_4^{2-}$	9.53		9.53			9.52	9.50	9.48						
SO_4^{2-}				11.50				11.48			11.43	11.38	11.27	

* Analyte retention time is concentration dependent for most anions. Retention time increases with increasing concentration for chloride. Retention time decreases with increasing concentration for bromide, nitrate, ortho-phosphate and sulfate.

EXAMPLE ION CHROMATOGRAM

cal std 4 IC stds 9001/9002

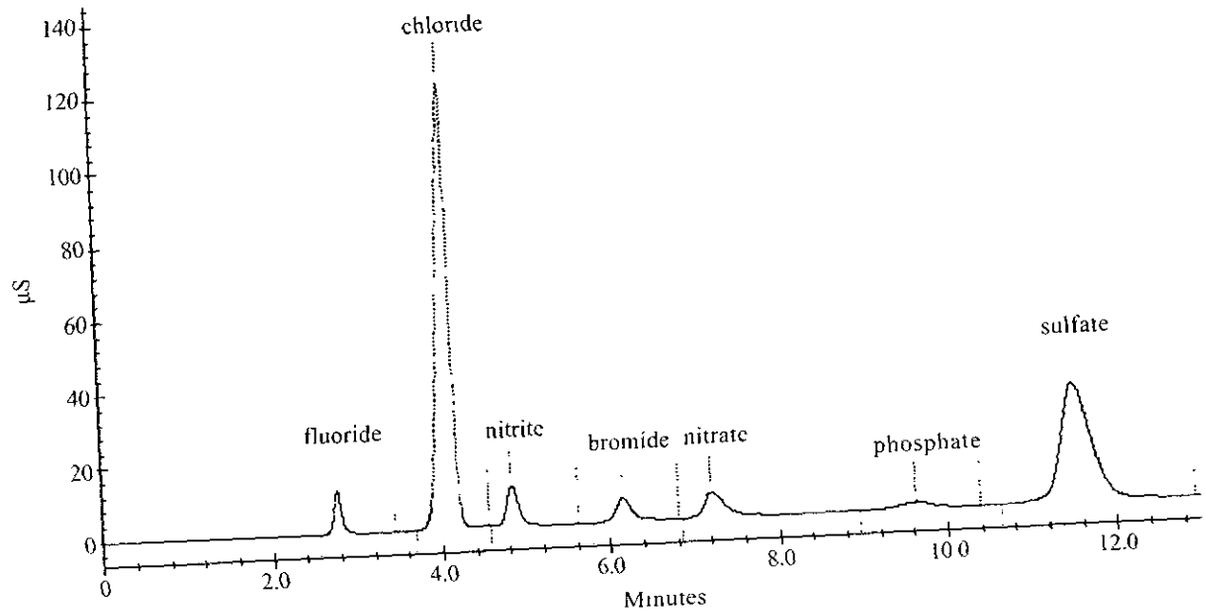


Figure #1

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Implementation Date: 03/02/01

SOP No. NC-WC-0006
Revision No. 4
Revision Date: 02/06/01
Page 1 of 13

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: ALKALINITY (TOTAL)

(SUPERSEDES: REVISION 3, REVISION DATE 04/04/00)

Prepared by: Angela Serra — 02/08/01 Date

Reviewed by: Technology Specialist — 02/08/01 Date

Approved by: Quality Assurance Manager — 2/15/01 Date

Approved by: Environmental Health and Safety Coordinator — 2-16-01 Date

Approved by: Laboratory Director — 2-20-01 Date

Proprietary Information Statement:

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TABLE OF CONTENTS

1. SCOPE AND APPLICATION

1.1. This method is applicable for the determination of total alkalinity in drinking, surface, saline, domestic, and industrial waters and wastewaters. It is also applicable to the determination of water-soluble alkalinity in solid samples if they have been prepared according to NC-WC-0073. It is based on EPA Method 310.1 and Standard Methods 2320B. The working linear range is 5 to 1000 mg/L.

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

1.3. QuantIMs reference for total alkalinity is VC (310.1) and LV (2320B).

2. SUMMARY OF METHOD

2.1. An unaltered sample is titrated to an electrometrical endpoint of pH 4.5. **The sample must not be filtered, concentrated, or altered in any way.**

3. DEFINITIONS

3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM), current version.

4. INTERFERENCES

4.1. Method interference's may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Samples with salts of weak organic and inorganic acids and greases or oils will interfere with pH measurements.

4.3. The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 mL.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive: Sulfuric Acid**

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL NORTH CANTONassociate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Alkalinity – Manual

6.1.1. Stir plate and stir bars

6.1.2. Graduated cylinders: various

6.1.3. Beakers: various

6.1.4. Buret: Class A 25 mL or 50 mL (preferred)

6.2. Alkalinity - Automated

6.2.1. Autotitrator

6.2.2. 50 mL centrifuge tubes

6.3. Alkalinity – Manual and Automated

6.3.1. pH meter and electrode(s) with temperature compensation

6.3.2. Volumetric pipettes: various

6.3.3. Autopipettor and disposable tips

6.3.4. Top loading balance: Capable of accurately weighing ±0.01 g

6.3.5. Volumetric flasks: various

6.3.6. Oven

6.3.7. Desiccator

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. 0.02 N Sulfuric Acid: reagent grade, purchased, standardized monthly.

7.1.2. Sodium Carbonate (Na_2CO_3): standard grade, dry overnight in 180°C oven and cool in a desiccator or purchased primary standard grade.

7.1.3. Sodium Carbonate Solution: Add 2.50g of Na_2CO_3 (record exact weight of Na_2CO_3 used) to a 1000mL volumetric flask and dilute to volume with reagent water. Mix well.

7.2. Standards

7.2.1. Target Calibration Standard

7.2.1.1. pH Buffers: 4, 7, and 10 (Manufactured)

7.2.2. Laboratory Control Sample

7.2.2.1. Alkalinity Standard, 25,000 mg/L $CaCO_3$, purchased or other commercially available reference solutions.

7.2.3. Matrix Spike Standard

7.2.3.1. Alkalinity Standard, 25,000 mg/L $CaCO_3$, purchased

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. The holding time is fourteen days from sampling to analysis.

8.4. The bottle must be filled with no headspace and provided in a separate container.

8.5. Do not open sample bottle before analysis. If other tests are to be performed from the same bottle, Alkalinity must be determined first. This is dependent on the client actually sending a separate bottle for alkalinity.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including

preparation and analysis. The method blank is used to identify any system and process interference's or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A reagent water blank consisting of 50 mL of reagent water and all other reagents added to samples within the analytical batch is analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. An LCS consisting of 1mL of the 25,000 mg/L alkalinity standard and 50 mL reagent water or other commercially available reference solution is analyzed with each analytical batch of samples.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. Corrective action will be reprepparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. An MS/MSD consisting of 1 mL of the 25,000 mg/L alkalinity standard and 50 mL of the sample will be analyzed.

9.4.3. Corrective action for MS/MSDs

9.4.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.3.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as DIL (diluted out).

9.4.3.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.5. QC Acceptance Criteria

9.5.1.1. Control limits are established by the laboratory as described in NC-QA-0018.

10. CALIBRATION AND STANDARDIZATION

10.1. Instrument Directions

10.1.1. Calibrate the pH meter according to the manufacturer's specifications. See pH Electrode Method SOP # NC-WC-0010.

10.2. Initial Calibration

10.2.1. The pH meter is calibrated everyday with the 4 and the 7 calibration buffers and is verified at the beginning of the run by using the 10 buffer. The pH buffers should bracket the sample concentration.

10.3. Continuing Calibration

10.3.1. The pH meter is checked every ten readings with a midrange (pH 7) buffer to ensure the calibration remain linear. The acceptance range for the calibration check is 7 ± 0.05 pH units or recalibration is necessary.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. For solids preparation, see SOP NC-WC-0073.

11.3.2. No preparation is necessary for water samples.

11.4. Standardization

11.4.1. To standardize 0.02 N sulfuric acid, titrate 50 mL reagent water and 0.125 g sodium carbonate (weighed accurately and recorded) with 0.02 N H_2SO_4 to a pH of 4.5. This should be performed monthly or on a new lot of acid (whichever is more frequent). Calculate as follows:

$$N = \frac{A \times 1000}{53.00 \times B} \text{ (manual)}$$

$$N = \frac{A \times 1000}{53.00 \times B} \times \frac{20}{50} \text{ (Autotitrator)}$$

A=gNa_2CO_3

B=mL .02 N H_2SO_4 titrant

11.5. Repeat standardization two or three more times. Record standardization in the calibration logbook.

11.6. Sample Analysis – Manual

11.6.1. Do not shake sample.

11.6.2. Record the initial pH prior to sample analysis

11.6.3. Record the initial pH prior to sample analysis. Use a sufficiently large volume of titrant (>20 mL in a 50 mL buret) to obtain good precision while keeping the volume low enough to permit a sharp end point

11.6.4. Place 50 mL of sample, or an aliquot diluted to 50 mL with reagent water, in a beaker. Begin mixing; measure and record initial pH of the sample. Titrate the sample to an endpoint of pH 4.5 with 0.02 N H_2SO_4. Record the volume of the titrant on the analytical logsheet. Samples requiring >50 mL titrant (> 75 mL using autotitrator) should be re-analyzed using less sample volume. Record dilution.

11.6.5. Use a sufficiently large volume of titrant (>20 mL in a 50 mL buret) to obtain good precision while keeping the volume low enough to permit a sharp end point.

11.7. Sample Analysis – Automated – Summary

11.7.1. The samples are analyzed on the autotitrator for Total Alkalinity.

11.7.2. Do not shake sample.

11.7.3. Place 50 mL of sample, or an aliquot diluted to 50 mL with reagent water, in a 50 mL centrifuge tube. See Manufacturer's information for operating instructions.

11.7.4. If a dilution of the sample was done change the volume on the schedule to reflect the dilution.(based on a 20 mL sample inject) For alkalinity the dilution factor will be taken into account in the final calculation. Do not manually multiply the dilution unless it was not typed into the schedule.

11.7.5. After the results have been gathered from the instrument make sure to check the pH of all the samples. If a sample has an initial pH of >4.5 and the Total Alkalinity is zero, the sample must be diluted and reanalyzed.

11.8. Analytical Documentation

11.8.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.8.2. All standards are logged into a department standard logbook. All standards are assigned a unique number for identification. The supervisor or designee reviews logbooks.

11.8.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.8.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. $$\textit{Alkalinity, mg/L } CaCO_3 \textit{ to pH 4.5} = \frac{A \times N \times 50{,}000}{mL \textit{ of sample}}$$

12.2. $$\text{LCS \%} = \frac{mg / L}{500 \textit{ (true)}} \times 100$$

$$\text{MS/MSD \%} = \frac{B - C}{500 \textit{ (true)}} \times 100$$

Where:

A = mL of Titrant

N = Normality of Titrant

B = MS/MSD, mg/L

C = Sample, mg/L

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that an associate who has been properly trained in its use and has the required experience performs this procedure.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Acid waste must be collected in clearly labeled acid waste containers.

15.2. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan.

15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. EPA-600/4-79-020, Methods for Chemical Analysis of Water and Wastes, Revised March 1983, Alkalinity, Method 310.1.

16.1.2. Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992,Alkalinity Methods, 2320B.

16.1.3. EPA 600, Methods for Chemical Analysis of Water and Wastes, pH, Method 150.1.

16.2. Associated SOPs

16.2.1. Solid Extraction for Wet Chemistry Parameters, NC-WC-0073.

16.2.2. pH Electrode Method for Wet Chemistry Parameters, NC-WC-0010.

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) for undiluted samples is 5 mg/L $CaCO_3$.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method Deviation

17.2.1. A fixed endpoint of 4.5 is used for all samples since the sample concentration is often unknown.

17.2.2. The Sodium Carbonate (Na_2CO_3) is dried at 180°C overnight instead of at 250° C for 4 hours.

17.2.3. The standard acid solution is not boiled gently for 3-5 minutes under a watch glass cover.

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Implementation Date 7-18-03

SOP No. NC-WC-0060
Revision No. 3
Revision Date: 06/17/03
Page 1 of 19

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: SULFIDE

(SUPERSEDES: REVISION 2; DATED 09/17/02)

Prepared by: Melissa A. Fuller-Gustafson 7/14/03
Date

Reviewed by: Angela Durla 7/11/03
Technology Specialist Date

Approved by: Beth Kimbrel 7/14/03
Quality Assurance Manager Date

Approved by: Deborah Budd 7/17/03
Environmental Health and Safety Coordinator Date

Approved by: Gail Ann Cook 7/18/03
Laboratory Director Date

Proprietary Information Statement:

TABLE OF CONTENTS

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of the concentration of Sulfide in waters, liquids, solids, and sludges. It is based on SW846 Method 9030B and Methods for Chemical Analysis of Water and Wastes (MCAWW) 376.1. The working range is 1 to 30 mg/L for waters and 10-650 mg/kg for solids and sludges.

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

1.3. The associated QuantIMS method codes are TV (9030B) and CT (376.1).

2. SUMMARY OF METHOD

2.1. For acid soluble sulfide samples, separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70^0C and the hydrogen sulfide (H_2S) which is formed, is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate scrubbing bottles where it is precipitated as zinc sulfide.

2.2. For acid-insoluble sulfide samples, separation of sulfide from the sample matrix is accomplished by suspending the sample in concentrated hydrochloric acid by vigorous agitation. Tin (II) chloride is present to prevent oxidation of sulfide to sulfur by the metal ion (as in copper (II)), by the matrix, or by dissolved oxygen in the reagents. The prepared sample is distilled under acidic conditions at 100^0C under a stream of nitrogen. Hydrogen sulfide gas is released from the sample and collected in gas scrubbing bottles containing zinc(II) and a strong acetate buffer. Zinc sulfide precipitates.

2.3. An excess of iodine is added to a sample which oxidizes the Sulfide to sulfur under acidic conditions. The excess iodine is back titrated with sodium thiosulfate.

3. DEFINITIONS

3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM).

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis

by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Reducing substances such as thiosulfite, sulfites, and various organic compounds cause interferences, but treatment with zinc acetate solution will eliminate some of these interferences. (Use approximately 15 drops of 2 N zinc acetate per 500 mL of sample if not already preserved with it.)

4.3. Samples that contain strong oxidizers or reducers will interfere with this method.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive: Hydrochloric Acid, Sodium Hydroxide, and Sulfuric Acid.**

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Volumetric pipettes: various

6.2. Buret: 25 mL Class A

6.3. Erlenmeyer flasks: 500 mL

6.4. Graduated cylinder: 250 mL

6.5. Top loading balance: capable of accurately weighing ± 0.01 g

6.6. Volumetric flasks: various

6.7. Vacuum pump, filter and flask

6.8. Whatman 934-AH filters

6.9. Distillation apparatus containing: 250 mL addition funnel, 500 mL – 3-neck reaction flask, sparging tube and 1 – 500 mL Erlenmeyer Flask.

6.10. Stirring / Hot Plates

6.11. Crystallizing dishes

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. (1:1) Hydrochloric Acid: Add 250 mL concentrated hydrochloric acid (HCl) to 250 mL of reagent water.

7.1.2. Starch Indicator: Add 10 mL of reagent water to 5 g starch (potato) and mix. Add starch mixture to 500 mL of boiling reagent water. Mix, cool, and store in a well-labeled squirt bottle. Alternately, use purchased starch solution.

7.1.3. 0.025 N Sodium Thiosulfate (stored in dessicator): Add 0.4 g NaOH and 6.205 g of sodium thiosulfate ($Na_2S_2O_3 \bullet 5H_2O$) to 500 mL of reagent water in a 1 liter volumetric. Dilute to volume with reagent water. Store in a dark container. Also available commercially.

7.1.3.1. Standardization of 0.025 N Sodium Thiosulfate Solution: *To make 0.025N Biodate Solution, dissolve 0.462 g $KH(IO_3)_2$ in 500 mL with reagent water. Weigh 2 g KI in a 500 mL Erlenmeyer flask. Add 100 to 150 mL reagent water, 5 drops H_2SO_4 and 20 mL biodate solution using a volumetric pipet. Dilute to 200 mL with reagent water. Titrate with Sodium Thiosulfate. When a pale straw yellow color is reached, add 1-2 mL starch. Continue titrating from a blue to a clear end point.

*Note: Biodate Solution may be purchased.

Calculation

$$Na_xS_2O_3\ Normality = \frac{(a)\ (b)}{c}$$

a = *mLs Biodate (20 mL)*

b = *Normality Biodate (0.025N)*

c = *mLs of $Na_2S_2O_3$ used to titrate* ***Repeat two more times***

7.1.4. 0.0282 N Iodine Solution: Add 20 g KI (potassium iodide) and 3.2 g iodine to a 1 liter volumetric flask. Add 500 - 700 mL of reagent water and dissolve. Dilute to volume with reagent water. Store in a dark container. Also available commercially.

7.1.4.1. Standardization 0.025 N Iodine Solution: Perform three method blanks daily. Refer to method blank section in SOP.

Calculation

$$Normality\ Iodine = \frac{(Normality\ Na_2S_2O_3)(mL\ of\ titrant\ Na_2S_2O_3)}{20\ mL\ Iodine}$$

7.1.5. 2N Zinc Acetate: Dissolve 220 g of zinc acetate in 870 mL of reagent water and dilute to 1 liter with reagent water.

7.1.6. Formaldehyde (37% solution), CH_20). This solution is commercially available.

7.1.7. Zinc Acetate for the Erlenmeyer flasks:

7.1.7.1. For acid-soluble Zinc: Zinc acetate solution (approximately 0.5M). Dissolve 110g Zinc acetate, dihydrate $NaC_2H_3O_2$, in 800 mL of reagent water. Add 1 mL concentrated hydrochloric acid and dilute to 1 liter.

7.1.7.2. For acid-insoluble sulfides: Zinc acetate/sodium acetate buffer. Dissolve 100 g sodium acetate, $NaC_2H_3O_2$, and 11 g zinc acetate dihydrate in 800 mL of reagent water. Add 1 mL concentrated hydrochloric acid and dilute to 1 liter. The resulting pH should be 6.8

7.1.8. Sulfuric acid – 50%. Place 450 mL of reagent water in a volumetric flash. **Slowly** add 500 mL concentrated Sulfuric Acid (H2SO4). **Use extreme caution – this is an exothermic reaction and will create excess heat**. This solution is commercially available.

7.1.9. Hydrochloric Acid, 9.8N, for **acid-insoluble sulfides**: Place 200 mL of reagent water in a 1-liter beaker. Slowly add concentrated HCl to bring the total volume to 1 liter.

7.1.10. Tin (II) chloride, $SnCl_2$, granular

7.2. Standards

7.2.1. Laboratory Control Sample

7.2.1.1. 2000 ppm Sulfide: Add 3.5 g of sodium sulfide to 100 mL of reagent water in a 250mL volumetric flask. Dilute to volume with reagent water. The sulfide standard must be verified each working day. If the resulting value is <75% of the original standard, a new solution must be prepared.

7.2.2. Matrix Spike Standard

7.2.2.1. Prepare a midrange matrix spike standard as described in 7.2.1 for use as a MS/MSD.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Waters are preserved to a pH > 9 with NaOH and zinc acetate. Non-water samples are unpreserved. All matrices are stored at 4°C ± 2°C in plastic or glass containers.

8.2. The holding time is seven days from sampling to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A reagent water blank consisting of 250 mL of reagent water must be analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A midrange LCS is prepared by adding 2.5 mL for Method 376.1 and 1.0 mL for Method 9030B (water samples) or 1.0 mL (solid samples) of 2000ppm sulfide standard to a flask. This standard must be analyzed with each analytical batch of samples.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.3. Corrective action will be reprepareation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. A MS/MSD consisting of 30 g or 250 mL of the sample and 2.5 mL for Method 376.1 or 1.0 mL for Method 9030B of 2000 ppm sulfide standard should be analyzed with every 20 samples.

9.4.3. Corrective action for MS/MSDs

9.4.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.3.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page "NC The recovery and/or RPD were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."

9.4.3.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the laboratory limits.

9.5. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest is version easily accessible via the LIMs (QC Browser program).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021.

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Water Samples Method 376.1

11.3.1.1. Using the vacuum apparatus, filter 250 mL (or a lesser aliquot) of well homogenized sample. Discard the filtrate and analyze the filter pad and solids following section 11.4. Record volume filtered on the analytical logsheet.

11.3.2. Aqueous Sample Method 9030B

11.3.2.1. For an efficient distillation, the mixture in the distillation flask must be of such a consistency that the motion of the stirring bar is sufficient to keep the solids from settling. The mixture must be free of solid objects that could disrupt the stirring bar. Prepare the sample using one of the procedures in this section then proceed with the distillation step.

11.3.2.2. If the sample is aqueous, shake the sample container to suspend any solids, then quickly decant the appropriate volume (250 mL) of the sample to a graduated cylinder. Transfer the contents of the graduated cylinder into the reaction flask.

11.3.2.3. If the sample is aqueous, but contains a large proportion of solids, the sample may be roughly separated by phase and the amount of each phase measured and weighed to the nearest milligram into the distillation flask in proportion to their abundance in the sample. Reagent water may be added up to a total volume of 250 mL.

11.3.3. Solids and Waste Samples, Method 9030B

11.3.3.1. Weigh out 30 g +/- 0. 1 g of homogenized sample and put into the reaction flask.

11.3.3.2. Samples that are not water miscible (oils, various solvents) cannot be analyzed using this method.

11.3.4. 9030B Distillation

11.3.4.1. Acid Soluble Sulfides:

11.3.4.1.1. Add 30g +/- 0.1g of solid sample plus 200 mL of reagent water or 250 mL of aqueous sample and a stir bar to the reaction flask

11.3.4.1.2. Attach the reaction flask to the distillation apparatus such that the bottom of the reaction flask does not touch the bottom of the crystallizing dish (submerge approximately 1/3 of the flask in the warm water).

11.3.4.1.3. Add 100 mL of 50% H2SO4 (7.1.8) to the addition flask and place in the center neck of the reaction flask. Attach the nitrogen flow line to the top of the addition flask.

11.3.4.1.4.Prepare one (1) gas trap bottles for each distillation setup by adding 200 mL of reagent water, 40 mL of zinc acetate buffer (7.1.7.1) and 10 mL of formaldehyde (7.1.6) to each trap.

11.3.4.1.5.Connect the trap and insert the trap arm into the right neck of the reaction flask. Turn on the nitrogen to approximately 5 psi and adjust the flow to 3 – 5 bubbles per second and purge for 15 minutes.

11.3.4.1.6.Add spike and LCS solution by removing the trap arm and pipetting the spike solution, below the surface of the water. Replace the trap arm and re-establish the flow of nitrogen, purge for 5 minutes.

11.3.4.1.7.Open the addition funnel to add the sulfuric acid (7.1.8) drop by drop. Do not open the stop cock fully. Distill the sample for 90 minutes, maintaining 70^0C in the water bath.

11.3.4.1.8.Fill the crystallizing dish with 650 – 700 mL of reagent water and place on the hotplate/stirrer. Turn on the hotplate to a setting of "6" for approximately 15 – 20 minutes. Turn down to a setting of "4" to maintain a temperature of 70^0C, +/- 5^0C.

11.3.4.2.Acid-Insoluble Sulfide:

11.3.4.2.1.As the concentration of HCl during distillation must be within a narrow range for successful distillation of H2S, the water content must be controlled. It is imperative that the final concentration of HCl in the distillation flask be about 6.5N and that the sample is mostly suspended in the fluid by the action of the stirring bar. This is achieved by adding 50 mL of reagent water, including water in the sample, 100 mL of 9.8N HCl, and the sample to the distillation flask. Solids which absorb water and swell will restrict fluid motion and, therefore, lower recovery will be obtained. Such samples should be limited to 25 g dry weight.

11.3.4.2.2.If the matrix is aqueous, then a maximum of 50 g of the sample may be used. No additional water may be added.

11.3.4.2.3.If the matrix is dry solid, use 30 g +/- 0.1 g of the sample and add 50 mL of reagent water.

11.3.4.2.4.Add 5 g SnCl to each distillation flask

11.3.4.2.5.Assemble the distillation apparatus. Place 200 +/- 4.0 mL of zinc acetate/sodium acetate buffer solution and 10.0 mL +/- 2.0 mL of 37% formaldehyde in each Erlenmeyer flask. Add 40 mL DI water.

11.3.4.2.6.Add 100 +/- 1.0 mL of 9.8N HCL to the addition funnel. Connect the nitrogen line to the top of the funnel and turn the nitrogen on to pressurize the dropping funnel headspace.

11.3.4.2.7.Set the nitrogen flow at 25 mL/min. The nitrogen in the Erlenmeyer flask should bubble at about five (5) bubbles per second. Purge the oxygen from the system for about 15 minutes.

11.3.4.2.8.Turn on the magnetic stirrer. Set the stirring bar to spin as fast as possible. The fluid should form a vortex. If not, the distillation will exhibit poor recovery. Add all the HCl from the dropping funnel to the flask.

11.3.4.2.9.Heat the water bath to the boiling point (100^0C). the sample may or may not be boiling. Allow the purged distillation to proceed for 90 minutes at 100^0C.

*Note: Watch water dishes so they don't go dry!

11.4. Sample Analysis

11.4.1. Summary

11.4.1.1.Excess iodine is added to a sample and under acidic conditions is back titrated with sodium thiosulfate from a blue to a clear color.

11.4.2. Sample Analysis Procedure

11.4.2.1.Method 376.1: Place the filter pad from the filtered water sample in a 500 mL Erlenmeyer flask. At this time, add any spiking solutions if necessary for the filtered water samples. Add 20.0 mL .028 N Iodine solution and 1-2 mL 1:1 HCl solution (watch for fumes). Check the pH prior to titration to make sure it is less than 2. If the pH is not <2, add additional acid. Add 250 mL reagent water only for the water samples and mix. Add 1 squirt (1-2 mL) of starch indicator and mix. Titrate from blue to clear

with .025 N sodium thiosulfate titrant. Record the amount of titrant used on the analytical logsheet.

Note: Some matrices may be turbid or colored and the color change from blue to clear may not be easily seen. In this case, look for a shade change.

11.4.2.2. 9030B/9034 Titrations: Titrate the scrubber solution in the Erlenmeyer. Add 20 mL of 0.028 N iodine solution under the liquid level in the Erlenmeyer, and 1-2 mL of 1:1 HCl solution. (More HCl is needed for insoluble 9030B.) Check the pH prior to titration to make sure it is less than 2. Add 1 squirt of starch indicator and mix. Titrate from blue to clear with .025 N sodium thiosulfate titrant.

*Note: Because of the buffer and the formaldehyde, the titration will take between 15 – 30 minutes. Add titrant slowly to allow the reaction to take place. Overtitrating could be an issue if the titrant is added too quickly.

11.4.2.3. After adding 20 mL iodine, the color should be orange/red. If the color remains yellow, add additional 10 mL aliquots until the orange/red color persists (adjust the calculation accordingly). If the sample requires more than 60 mL of iodine, the sample must be re-prepped at a smaller dilution. The iodine should turn a yellow-orange color when added to the sample after the addition of the reagent water. If it does not, the sample may be high in sulfide and less sample should be used, or more iodine for 9030B.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, which may be in electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2. All standards are logged into a department standard logbook. All standards are assigned a unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

$$\textit{Sulfide, mg / L or mg / kg} = \frac{\textit{[(A x B) - (C x D)] x 16,000}}{\textit{mL or g of sample used}}$$

Where:

A = ***mL of iodine solution***

B = ***Normality of iodine solution***

C = ***mL of sodium thiosulfate titrant***

D = ***Normality of sodium thiosulfate titrant***

$$\textit{Sulfide, mg / L or mg / kg} = \frac{\textit{(20 - mL titrant) x 400}}{\textit{mL or g of sample used}}$$

12.1.1.

$$LCS\,\%\ \text{Recovery} = \frac{\text{mg/L (from 12.1.1)}}{\text{20 (true)}} \times 100$$

Note: The true value of the standard is determined daily.

12.1.2.

$$\text{MS/MSD \% Recovery} = \frac{\text{A - B}}{\text{20 (waters) or 1000 (solids)}} \times 100$$

Where:

A = ***(20 - mL titrant for MS/MSD) x 400***

B = ***Concentration from 12.1.1 x mL or g of sample used***

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All aqueous sample preparations can be rinsed down the drain with copious amounts of water.

15.2. Solvent waste must be disposed of in clearly labeled waste cans.

15.3. Acid waste must be collected in clearly labeled acid waste containers.

15.4. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.5. Refer to the Laboratory Sample and Waste Disposal plan.

15.6. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods of Evaluating Solid Waste, Third Edition, Sulfide, Method 9030B.

16.1.2. EPA 600, Methods for Chemical Analysis of Waters and Wastes, Sulfide (Titrimetric, Iodine), Method 376.1

16.1.3. Standard Methods Eighteenth Edition, Sulfide Method 4500-S^2-E

16.1.4. STL North Canton Laboratory Quality Manual (LQM), current version.

16.1.5. STL Quality Management Plan (QMP), current version.

16.1.6. SW846, Test Methods of Evaluating Solid Waste, Third Edition, Titrimetric Procedure for Acid-soluble and Acid-insoluble Sulfides, Method 9034.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limits (RL) are 1 mg/L for waters and 50 mg/kg for solids.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method Deviations

17.2.1. The lab does not perform the distillation procedure described in Method SW846 9030A.

17.2.2. The laboratory uses one collection flask instead of two.

17.2.3. The laboratory does not titrate the sample in the original container as specified in Method 376.1

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STL Buffalo

LABORATORY STANDARD OPERATING PROCEDURES

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SOP No. AWC-VFA-20	Revision No. 1	Date February 4, 2004	Page 1 of 13

TITLE: Volatile Fatty Acids
Supercedes: Revision 0

REVIEWED & APPROVED BY:	Signature	Date
Christopher Oprandi, Laboratory Director	Christopher Oprandi	2/5/04
Verl D. Preston, Quality Manager	Verl D. Preston	2/5/04
Peggy Gray-Erdmann, Supervisor	Peggy Gray-Erdmann	2/10/04

1.0 IDENTIFICATION OF TEST METHODS

1.1. Volatile Fatty Acids are determined using Dionex proprietary method. This method is a modification to Standards Methods for the Examination of Water and Waste Water 20th ed., Method 5560 Organic and Volatile Acids.

2.0 APPLICABLE MATRIX

2.1. This method is applicable to surface water, groundwater, wastewater, drinking waters and soils.

3.0 REPORTING LIMIT

3.1. The reporting limit for each acid is listed below:
3.1.1. Acetic Acid – 1 mg/L

3.1.2. Propionic Acid – 1 mg/L

3.1.3. Butyric Acid – 1 mg/L

3.1.4. Lactic Acid – 1 mg/L

3.1.5. Formic Acid – 1 mg/L

3.1.6. Pyruvic Acid -- 1 mg/L

3.2. MDLs are calculated every year in accordance with method specification and kept on file with the QA department.

4.0 SCOPE AND APPLICATION

4.1. Ion Chromatography provides a single instrumental technique that may be used for the measurement in environmental samples of the common Volatile Fatty acids or Organic acids. Fatty acids are low-molecular weight carboxylic acids. Identification and quantification is performed by Ion chromatography. Separation is accomplished by an ion-exclusion column. Peak sensitivity and lower reporting limits are obtained by using an eluent suppressor. The acids are then identified by conductivity detection.

5.0 SUMMARY OF TEST METHOD

5.1. A filtered aqueous sample is injected into an ion chromatograph with the use of an automated sampler. The sample merges with an eluent stream and is pumped through the system. The ion exchanger separates the acids of interest. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak area and comparing it to a calibration curve generated from known standards.

6.0 DEFINITIONS

6.1. Standard definitions can be found in section 3.0 of the STL Buffalo Laboratory Quality Manual.

6.2. VFA: Volatile Fatty Acid

7.0 INTERFERENCES

7.1. Interferences can be caused by substances with retention times that are similar to and overlap those of the acid of interest. Acids of high concentrations can interfere with the peak resolution of an adjacent acid. Diluting the sample can minimize overlap.

7.2. Method interferences may be caused by contaminants in the reagent water, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or an elevated baseline in the ion chromatograms.

7.3.1 All samples must be filtered through a 20um filter before injection. If particles contaminate the guard or analytical columns, follow the manufacturer's suggestions for cleaning, or simply replace the column.

8.0 SAFETY

8.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

8.2.1. This method uses weak carboxylic acids and heptafluorobutyric acid. All acids will be poured into water.

8.2.2. Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

8.3. PRIMARY MATERIALS USED

8.3.1. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Heptafluor-Butyric acid	Corrosive	NA	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain.
Fatty Acid Custom Mix 1000ppm in water	Corrosive	NA	May irritate eyes and/or skin. Irritates Respiratory tract. Low blood pressure. Dermatitis. Pulmonary edema. Lung damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

9.0 EQUIPMENT AND SUPPLIES

9.1. Ion chromatograph complete with all required accessories:

9.1.1. ICE-AS6 separator column capable of resolving weak organic acids.

9.1.2. AMMS-ICE suppressor.

9.1.3. Conductivity detector with temperature control and separate working and reference electrodes.

9.1.4. Pump able to deliver 1.2 ml/min of constant flow rate.

9.1.5. Data collection and analysis system.

9.1.6. Automated sampler.

9.2. Various laboratory glassware such as Class A graduated cylinders, syringes, volumetric flasks and pipettes.

9.3. 10 ml syringes and 0.2 um syringe filters for colored samples

9.4. Analytical balance, capable of weighing to the nearest 0.0001g.

9.5. Filter caps for clean samples purchased from Dionex

9.6. 5 ml sample vials purchased from Dionex

10.0 REAGENTS AND STANDARDS

10.1. Sample bottles: Glass or polyethylene bottles of sufficient volume to allow replicate analyses of anions of interest.

10.2. Reagent water: Distilled or deionized water free of the anions of interest. Water should contain particles no larger than 0.20 microns.

10.3. Regenerant Concentrate (TetraButylAmmonium Hydroxide TBAOH) from VWR catalog# (JTV365-7) 0.4M water solution.

10.3.1 Regenerant solution (10mM): Add 50ml of 0.4M TBAOH into 2L reagent water.

10.4. Eluent Concentrate (Heptafluorobutyric acid): 99% Heptafluorobutyric acid is purchased from Aldrich. Catalog # 16,419-4

10.4.1. Eluent Solution (1.0mM.): Weigh 0.21g of the Heptafluorobutyric acid (10.4) to 1 liter with reagent water or 250ul into 2 liter

SOP No. AWC-VFA-20	Revision No. 1	Date February 4, 2004	Page 5 of 13

TITLE: Volatile Fatty Acids
Supercedes: Revision 0

10.5. Multi analyte Ion Chromatography Custom Standards purchased from Restek & Supelco Scientific. Custom Mix contains 1000mg/l of the following acids: Acetic, Propionic, Butyric, Lactic, Formic, and Pyruvic. The standard source from Supelco is used for the calibration curve (10.6) and the standard source from Restek is used for the ICV/ CCV/LCS Solutions and the matrix spikes (10.7, 10.8, 10.9, 10.10).

10.6. Calibration standards: all are made from dilutions of the Multi Element IC Standards in reagent water.

10.6.1. Prepare the calibration standards for a 5-point curve by measuring the following volumes into a 25 ml Class A volumetric. Bring to the final volume of 25 ml with reagent water.

	Level 1	Level 2	Level 3	Level 4	level 5
Stock solution (1000 mg/L)	25ul	50ul	125ul	250ul	1.25ml
Final Volume	25ml	25ml	25ml	25ml	25ml

10.6.2 The final concentrations of each anion in the 5 calibration points are summarized below.

	Level 1 (mg/L)	Level 2 (mg/L)	Level 3 (mg/L)	Level 4 (mg/L)	Level 5 (mg/L)
Formic	1	2	5	10	50
Propionic	1	2	5	10	50
Butyric	1	2	5	10	50
Lactic	1	2	5	10	50
Formic	1	2	5	10	50
Pyruvic	1	2	5	10	50

10.7. ICV/CCV/LCS, MS and SD (MSD) solution: 500ul of the Multi Element IC Standard diluted to 100ml with reagent water. The final concentration for each acid in the solution is as follows:

	ICV & CCV/LCS
Acetic	5 mg/L
Propionic	5 mg/l
Butyric	5 mg/l
Lactic	5 mg/l
Formic	5 mg/l
Pyruvic	5 mg/l

TITLE: Volatile Fatty Acids
Supercedes: Revision 0

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

11.1. Samples should be shipped and stored in 40 mL glass amber vials at 4 ± 2 degrees C. Samples should be analyzed for VFA within 28 days of collection.

11.2. Soil will follow the same preservation and holding times as the water samples, starting from the time of extraction. Soils should be collected in 4 oz. or 8 oz. wide mouth amber jars.

12.0 QUALITY CONTROL

12.1. Before analyzing samples, the laboratory must establish a method detection limit (MDL). The MDL is repeated every year.

12.2. Each group of sample analyses must be bracketed by an acceptable calibration verification sample and calibration blank. All quality control data should be maintained and available for easy reference or inspection.

12.3. Initial and Continuing Calibration Blank (ICB, CCB): To determine freedom from contamination, prepare one calibration blank (ICB) at the beginning of the analytical procedure and another (CCB) after every ten samples and at the end of the analytical procedure. The blank consists of 5 ml reagent water that gets the same treatment as the samples and standards. The blanks must be free of the analytes of concern at levels less than the STL Buffalo quantitation limit.

12.3.1. All blanks associated with USACE samples should be less than half the STL Buffalo quantitation limit for each anion.

12.4. Initial and Continuing Calibration Verification/Laboratory Control Sample (ICV/CCV/LCS): Prepare an ICV at the beginning of the analytical procedure and additional CCV/LCS after every ten samples and again at the end of the procedure. The recovery of the ICV/CCV/LCSs must be within 80-120% of the true value.

12.5. Sample Duplicate: Analyze either a Matrix Duplicate (MD) or a Matrix Spike Duplicate (MSD) with every batch of twenty or fewer samples. Acceptable RPD between replicate analyses should be less than 20%.

12.6. Matrix Spikes (MS) are to be run with every batch of 20 or fewer samples. Deviations may occur due to specific client, state, or protocol requirements. Spike 10ml of sample with 50ul of Multi-analyte Stock solution (1000mg/L) section 10.5.

13.0 CALIBRATION AND STANDARDIZATION

13.1. Prepare standard 5-point curve by plotting instrument response against concentration values.

13.1.1. Generate a linear regression curve. Do not force through zero and do not average in the origin.

13.1.2. A calibration curve may be fitted to the calibration solution concentration/response data using the manufacturer's software.

13.1.3. Acceptance criteria for the calibration curve is a correlation coefficient (R value) $\geq$0.995. If the R-value is less than 0.995, the calibration standards must be remade and a new curve analyzed.

13.1.4. New calibration curves must be run every three months or if the instrument falls out of calibration whichever is sooner

13.2. Initial Calibration Verification Solution prepared from a different standard source is analyzed immediately after the calibration curve to verify the accuracy of the curve. The recovery of the ICV must be within 80-120%.

14.0 PROCEDURE

14.1. System Equilibrium:

14.1.1. Set up the ion chromatograph as specified in the manufacturer's instructions.

14.1.2 Turn on and prime the pump.

14.1.3 Adjust the eluent flow rate to 1.2 $\pm$ 0.1 ml/min. Adjust Regenerant pressure to 5PSI. Adjust restrictor at the end of the regenerant waste line to allow for 3-5ml/min. flow.

14.1.4 Allow the system to come to equilibrium (15-20 minutes). A stable baseline indicates system equilibrium.

14.2. Sample analysis:

14.2.1. For dirty samples filter sample through a pre-washed 0.2um pore diameter membrane filter. If sample is clean use 20um filter autosampler caps.

14.2.2. Fill autosampler vials with the sample to the fill line marked on the vial body (approximately 5 ml). Place vial cap into vial.

14.2.3. Place the filled vial into the sampler cassette and fully insert the cap using the insertion tool.

14.2.4. Place the filled cassettes into the automated sampler and start the run. Set sample run time to 64 minutes.

14.2.5. Check data for any needed dilutions and calculate percent recovery of check standards and sample spikes. Any data from samples that were diluted will have to be multiplied by the dilution factor before reporting.

14.3. Column cleanup procedure

14.3.1. Disconnect the suppressor from the analytical column. Reverse the order of the guard and analytical column in the eluent flow path. Double check that the eluent flows in the direction designated on each of the column labels.

14.3.1.1. CAUTION: When cleaning an analytical column and a guard column in series, ensure that the guard column is placed after the analytical column in the eluent flow path. Contaminants that have accumulated on the guard column can be eluted onto the analytical column and irreversibly damage it. If in doubt, clean each column separately.

14.3.2. Set the pump flow rate to 1.0 ml/min for the ICE-AS6 analytical.

14.3.3. Rinse the column for 15 minutes with reagent water before pumping the 0.1M oxalic acid over the column. Acetone can also be used to remove organics. Start with a 5% solution and increase up to 15%, but do not exceed 15%.

14.3.4. Pump the cleanup solution through the column for at least 60 minutes.

14.3.5. Rinse the column for 30 minutes with reagent water before pumping eluent over the column.

14.3.6. Equilibrate the columns with eluent before resuming normal operations for at least 30 minutes.

14.3.7. Reconnect the ASRS-Ultra to the analytical column.

14.4 Retention time (migration time) is the expected time retention time or migration time in minutes for the component. If the retention time is unknown, enter any number greater then zero. The correct retention time can be determined later from the first calibration run, and the component table then updated. In subsequent calibrations, PeakNet will automatically update the retention time. The Update Retention Time setting must be selected in the calibration Parameters dialog box.

15.0 CALCULATIONS

15.1. Using the computer and software packages, prepare a linear regression calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve.

The response factor produced from a linear equation best fits the detector's response. The equation used is shown below.

$$Y = K0 + K1 \times X$$

At least four points are needed to fit the equation: thus, the calibration must have at least four levels for all components.

The following values, used to calculate component amount, are determined automatically by the Method Editor and cannot be edited.

X= area
K0 indicates the Y intercept of the calibration curve.
K1 is the coefficient for the first-degree variable. When the fit type is linear, K1 indicates the slope of the calibration curve for the selected calibration level.

The equation for the calibration curve fit used to calculate the component amount is displayed at the bottom of the replicate page. The r2 value (Coefficient of Determination) for the component is shown at the bottom of the replicate page.

15.2. The analyst corrects the results for and dilution factors:

$$Xf = Xj * \text{Dilution Factor}$$

Where:
Xf = Final sample concentration
Xj = calculated concentration of sample at instrument

15.3. Report only those values that are less than the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

16.0 METHOD PERFORMANCE

16.1. The method detection limit (MDL) is to be performed every year in accordance with the specifications in 40 CFR 136, appendix B, and must demonstrate the ability to quantitate at or below the reporting limit for each acid. The current MDL is on file with the department supervisor and the QA Department.

17.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

17.1. Obtained ICV and CCV/LCS values must be within 80-120% of the true value.

17.2. Acceptance limits for sample spike recovery are based on the historical data and are statistically derived annually. They are maintained in the laboratory LIMs system. If the

lab calculated limits are wider than the method limits, the method limits of 80-120% are used for evaluation of sample spike acceptance.

17.3. Sample duplicates are required to have a calculated RPD $\leq$ 20.

17.4. ICB and CCB values must be less than the STL quantitation limit.

17.4.1. All blanks associated with USACE samples should be less than ½ the STL Buffalo quantitation limit for each anion.

18.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

18.1. If acceptance criteria are exceeded for any QC element, all related samples and check standards must be repeated.

19.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

19.1 If acceptable data can not be obtained, a Job Exception Form is to be filled out and turned in to the appropriate project manager in order to notify of the client.

19.2 Historical data review may be used to evaluate sample results.

20.0 WASTE MANAGEMENT/ POLLUTION PREVENTION

20.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for " Waste Management and Pollution Prevention."

20.2 Waste Streams Produced by the Method -The following waste streams are produced when this method is carried out.

20.2.1 Alkaline and/or acidic waste generated by the analysis. Dispose of this waste in the " A" waste container.

20.2.2 Contaminated plastic materials such as IC syringes, filters, caps and vials utilized for sample preparation. All plastic materials should be disposed of in the recycling containers located throughout the lab.

21.0 REFERENCE

21.1. Method 300.0, "Determination of Inorganic Anions by Ion Chromatography", Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, Ohio, Revision 2.1, August 1993

21.2. Method 5560, Standard Methods for the Examination of Water and Wastewater, 20th Edition,

21.3. Dionex application note #45, "Fatty Acid Analysis"

22.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

22.1. Analytical Run sequence

22.2. Wet Chemistry Batch Summary & Data Review Checklist

23.0 CHANGES FROM PREVIOUS REVISION

23.1 Changed the reporting limit of Butyric acid from 2 mg/L to 1 mg/L

23.2 Changed the concentration of the regenerant solution from 4 mM to 10 mM

23.3 Changed the concentration of the eluent solution from 0.6 mM to 1.0 mM

23.4 Removed MSD reference and added specific recipe for MS in section 12.6

23.5 Added 64 minute run time to section 14.2.4

TITLE: Volatile Fatty Acids
Supercedes: Revision 0

22.1 Analytical Run Sequence

LCS/CCV
ICB
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
CCV
CCB
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample dup
Sample Spike
CCV
CCB

TITLE: Volatile Fatty Acids
Supercedes: Revision 0

22.2 Wet Chemistry Batch Summary & Data Review Summary

WET CHEMISTRY BATCH SUMMARY

Parameter _____ Method _____ Batch #_____

Comment #	Comment
1	NA
2	Sample(s) was diluted for matrix interference.
3	Sample(s) was diluted for excessive foaming/
4	Sample(s) was diluted for turbidity.
5	NA
6	NA
7	NA
8	Sample(s) was diluted for high concentration of target analyte
9	Sample(s) was diluted for turbidity.
10	Sample(s) was diluted for color.
11	There was insufficient volume for a lower dilution.
12	Sample(s) was diluted for viscosity.
13	Sample(s) was diluted for other reason (detail required)
14	Sample(s) required re-run to verify result.
15	Sample(s) requires re-run to verify deviation from historical result.
16	Sample(s) requires re-run for CCB failure.
17	Sample(s) affected by elevated CCB are greater than 10x detection limit.
18	Sample was colored.
19	Sample(s) was received outside of Holding Times.
20	Sample(s) contained a high amount of settleable material.
21	Sample(s) contained a high amount of suspended material
22	Sample(s) were centrifuged for turbidity.
23	There was insufficient volume for analysis of sample at method required volume.
24	There was insufficient volume for re-analysis of the sample(s).
25	There was insufficient volume for dilution of the sample(s).
26	There was insufficient volume for Dup/Spk.
27	Sample(s) was cloudy
28	See accompanying Job Exception Report.

Comments and Corrective actions

#_____ Sample(s)_____

#_____ Sample(s)_____

#_____ Sample(s)_____

#_____ Sample(s)_____

CCV/CCB Compliant? NA_____ YES_____ NO_____(see reason below)

Other_____

_____

_____

Technician _____ Date_____

2nd Review _____ Date_____ **Number of Reanalysis for this batch:**_____

Review _____ Date_____

WC Summary Rev 1 7-2003

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Implementation Date: 10/18/00

SOP No. CORP-IP-0004NC
Revision No. 1.1
Revision Date: 10/10/00

STL STANDARD OPERATING PROCEDURE

TITLE: TOXICITY CHARACTERISTIC LEACHING PROCEDURE

AND SYNTHETIC PRECIPITATION LEACHING PROCEDURE

(SUPERSEDES: REVISION 1, REVISION DATE 02/01/00)

Prepared by:		10/17/00 Date
Reviewed by:	Technology Specialist	10/17/00 Date
Approved by:	Quality Assurance Manager	10/17/00 Date
Approved by:	Environmental Health and Safety Coordinator	10-17-00 Date
Approved by:	Laboratory Director	10-17-00 Date

Proprietary Information Statement:

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Table of Contents

LIST OF APPENDICES

1. SCOPE AND APPLICATION

1.1. This SOP describes the application of the Toxicity Characteristic Leaching Procedure (TCLP), SW846 Method 1311. The Toxicity Characteristic (TC) of a waste material is established by determining the levels of 8 metals and 31 organic chemicals in the aqueous leachate of a waste. The TC is one of four criteria in 40 CFR Part 261 to determine whether a solid waste is classified as a hazardous waste. The other three are corrosivity, reactivity and ignitability. The TC Rule utilizes the TCLP method to generate the leachate under controlled conditions that were designed to simulate leaching through a landfill. EPA's "worst case" waste disposal model assumes mismanaged wastes will be exposed to leaching by the acidic fluids generated in municipal landfills. The EPA's model also assumes the acid/base characteristics of the waste will be dominated by the landfill fluids. The TCLP procedure directs the testing laboratory to use a more acidic leaching fluid if the sample is an alkaline waste, again in keeping with the model's assumption that the acid fluids will dominate leaching chemistry over time.

1.2. The specific list of TC analytes and regulatory limits may be found in Appendix A.

Note: The list in Appendix A does not include the December 1994 EPA rule for Universal Treatment Standards for Land Disposal Restrictions. Those requirements include 216 specific metallic and organic compounds and, in some cases, lower detection limit requirements (see 40 CFR 268.40). TCLP leachates are part of the new Universal Treatment Standards, but the conventional analytical methods will not necessarily meet the new regulatory limits. Consult with the client and with STL Technical Specialists before establishing the instrumental methods for these regulations.

1.3. This SOP also describes the application of the Synthetic Precipitation Leaching Procedure (SPLP) which was designed to simulate the leaching that would occur if a waste was disposed in a landfill and exposed only to percolating rain water. The procedure is based on SW846 Method 1312. The list of analytes for SPLP may extend beyond the toxicity characteristic compounds shown in Appendix A. With the exception of the use of a modified extraction fluid, the SPLP and TCLP protocols are essentially equivalent. Where slight differences may exist between the SPLP and TCLP they are distinguished within this SOP.

1.4. The procedure is applicable to liquid, solid, and multiphase wastes.

1.5. The results obtained are highly dependent on the pH of the extracting solution, the length of time that the sample is exposed to the extracting solution, the temperature during extraction,

and the particle size/surface area of the sample. These parameters must be carefully controlled.

1.6. The reporting limits are based on the individual samples as well as the individual analysis techniques. However, the sample is determined to be hazardous if it contains any analyte at levels greater than or equal to the regulatory limits.

1.7. If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the procedure need not be run. If the total analysis results indicate that TCLP is not required, the decision to cease TCLP analysis should be remanded to the client.

1.8. If an analysis of any one of the liquid fractions of the procedure leachate indicates that a regulated compound is present at such a high concentration that, even after accounting for dilution from the other fractions of the leachate, the concentration would be equal to or above the regulatory level for that compound, then the waste is hazardous and it may not be necessary to analyze the remaining fractions of the leachate. However, the remaining analyses should not be terminated without the approval of the client.

1.9. Volatile organic analysis of the leachate obtained using a bottle extraction, normally used for extractable organics and metals, can be used to demonstrate that a waste is hazardous, but only the ZHE option can be used to demonstrate that the concentration of volatile organic compounds is below regulatory limits due to potential analyte loss into the headspace during the bottle extraction.

2. SUMMARY OF METHOD

2.1. For liquid wastes that contain less than 0.5% dry solid material, the waste, after filtration through 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP leachate.

2.2. For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solids and stored for later analysis or recombination with the leachate. The particle size of the remaining solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. For TCLP, the extraction fluid employed for extraction of non-volatile analytes is a function of the alkalinity of the solid phase of the waste. For SPLP, the extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater the extraction fluid employed is a pH 4.2 solution. Two leachates may be generated: a) one for analysis of non-volatile constituents (semi-volatile organics, pesticides, herbicides and metals and/or b) one from a Zero Headspace Extractor (ZHE) for

analysis of volatile organic constituents. Following extraction, the liquid leachate is separated from the solid phase by filtration through a 0.6 to 0.8 μm fiber filter.

2.3. If compatible (i.e., multiple phases will not form on combination), the initial liquid filtrate of the waste is added to the liquid leachate and these are prepared and analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3. DEFINITIONS

3.1. "Leachate" is used to refer to the solutions generated from these procedures (TCLP, SPLP, deionized water leach).

3.2. "Wet Solids" is that fraction of a waste sample from which no liquid may be forced out by pressure filtration.

4. INTERFERENCES

4.1. Oily wastes may present unusual filtration and drying problems. If requested by the client and as recommended by EPA (see Figure 3), oily wastes can be assumed to be 100% liquid and analysis for total concentrations of contaminants will be performed. This applies specifically to samples containing viscous non-aqueous liquids that would be difficult to filter. Alternately, the oil may be subjected to pressure filtration. The portion that passes through the filter will be prepared and analyzed separately as an organic waste. The "wet solid" portion that remains behind on the filter will be subjected to leaching, prepared and analyzed. The results will then be mathematically combined.

4.2. Wastes containing free organic liquids (e.g., oil, paint thinner, fuel) usually require dilution prior to analysis to address the matrix interferences. In most instances this results in reporting limits elevated above the TCLP regulatory limits.

4.3. Solvents, reagents, glassware and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks as described in Section 9 and the individual determinative SOPs.

4.4. Glassware and equipment contamination may result in analyte degradation. Soap residue on glassware and equipment may contribute to this. All glassware and equipment should be rinsed very carefully to avoid this problem.

4.5. Phthalates may be eliminated by proper glassware cleanup and by avoiding plastics. Only glass, Teflon or Type 316 stainless steel tumblers may be used for leachates to be analyzed for organics. Plastic tumblers may be used for leachates to be analyzed for the metals.

4.6. Overexposure of the sample to the environment will result in the loss of volatile components.

4.7. Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include:
Methylene chloride

5.3.2. Chemicals known to be flammable are:
Methanol

5.3.3. The following materials are known to be corrosive:
Hydrochloric acid, nitric acid, sulfuric acid, acetic acid, sodium hydroxide

5.3.4. The following materials are known to be oxidizing agents:
Nitric Acid.

5.4. Gas pressurized equipment is employed in this procedure. Be sure all valves and gauges are operating properly and that none of the equipment, especially tubing, is over-pressurized. CAUTION: Do not open equipment that has been pressurized until it has returned to ambient pressure.

5.5. A rotary agitation apparatus is used in this procedure. Certain samples may break the glass jars used in the procedure. For these samples, extra caution, including plastic or polyethylene overwraps of the glass jar, may be necessary. Turning the jar or bottle sideways rather than tumbling end over end may also reduce the chance of breakage. If sideways tumbling is used, note this change in the logbook comment section.

5.6. Secure tumbler and extraction apparatus before starting rotary agitation apparatus.

5.7. During sample rotation, pressure may build up inside the bottle. Periodic venting of the bottle will relieve pressure.

5.8. Exposure to hazardous chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.9. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.10. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported immediately to a laboratory supervisor.

5.11. Due to the potential for ignition, flammability or production of noxious fumes, do not attempt to dry non-aqueous liquid samples in an oven. Use extended drying in a ventilation hood.

6. EQUIPMENT AND SUPPLIES

6.1. Extraction vessels

6.1.1. For volatile analytes - zero-headspace extraction (ZHE) vessel, gas-pressure actuated, Millipore YT3009OHW or equivalent (see Figure 2).

6.1.2. For metals - either borosilicate glass jars (2.5 L, with Teflon lid inserts) or 2.5 L HDPE (Nalgene or equivalent) bottles may be used.

6.1.3. For non-volatile organics - only borosilicate glass may be used.

6.2. Vacuum filtration apparatus and stainless steel pressure filtration apparatus (142 mm diameter), capable of 0 - 50 psi.

6.3. Borosilicate glass fiber filters, 0.6 - 0.8 µm (Whatman GF/F 14.2 cm, 9.0 cm, 4.7 cm, 0.7 µm or equivalent). When analyzing for metals, wash the filters with 1 N nitric acid and de-ionized water prior to use, or purchase pre-washed filters. Glass fiber filters are fragile and should be handled with care.

6.4. Rotary agitation apparatus, multiple-vessel, Associated Design and Manufacturing Company 3740-6 or equivalent (see Figure 1). The apparatus must be capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rpm.

6.5. ZHE Extract Collection Device: Gas-tight syringes, 50 or 100 mL capacity, Hamilton 0158330 or equivalent.

6.6. Top loading balance, capable of 0 - 4000 ± 0.01g (all measurements are to be within ± 0.1 grams).

6.7. pH meter and probe capable of reading to the nearest 0.01 unit, and with automatic temperature compensation.

6.8. pH probes.

6.9. Magnetic stirrer/hotplate and stirring bars.

6.10. VOA vials, 40 mL, with caps and septa.

6.11. Glass bottles, 1 liter, with Teflon lid-inserts.

6.12. Nalgene plastic bottles or equivalent, 1 liter.

6.13. Miscellaneous laboratory glassware and equipment.

7. REAGENTS AND STANDARDS

7.1. Reagent water for non-volatile constituents must be produced by a Millipore DI system or equivalent. For volatile constituents, water must be passed through an activated carbon filter bed (Milli-Q or tap water passed through activated carbon). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Hydrochloric acid, 1 N: Carefully add 83 mL concentrated reagent grade HCl to 800 mL reagent water, cool and dilute to 1 liter with reagent water. Cap and shake to mix well.

7.3. Sodium hydroxide, 1 N: Carefully add 40 g reagent grade NaOH pellets to 800 mL reagent water, stir until the pellets are completely dissolved, cool and dilute to 1 liter with reagent water.

CAUTION: Heat is generated during this process.

7.4. Acetic acid, glacial: concentrated, reagent grade liquid (HOAc).

7.6. pH calibration solutions: buffered to a pH of 4, 7, and 10. Commercially available.

7.5. TCLP Leaching Fluids

7.5.1. General Comments

7.5.1.1. The pH of both solutions listed below should be monitored daily and the pH probes are to be calibrated prior to use.

7.5.1.2. The leaching fluids MUST be prepared correctly. If the desired pH range is not achieved and maintained, the TCLP may yield erroneous results due to improper leaching. If the pH is not within the specifications, the fluid must be discarded and fresh extraction fluid prepared.

7.5.1.3. Additional volumes of extraction fluids listed below may be prepared by multiplying the amounts of acetic acid and NaOH by the number of liters of extraction fluid required.

7.5.2. TCLP Fluid #1: Carefully add 5.7 mL glacial acetic acid and 64.3 mL of 1 N NaOH to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. For 8 L of fluid use 45.6 mL glacial acetic acid and 514 mL 1N NaOH, dilute to 8 L with reagent water. When correctly prepared, the pH of this solution is 4.93 ± 0.05. The density of TCLP fluid #1 is 0.997 g/mL.

7.5.3. TCLP Fluid #2: Carefully add 5.7 mL glacial acetic acid to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. For 8 L of fluid use 45.6 mL glacial acetic acid, dilute to 8 L with reagent water. When correctly prepared, the pH of this solution is 2.88 ± 0.05. The density of TCLP fluid #2 is 0.997 g/mL.

7.6. Nitric acid, 50% solution: Slowly and carefully add 500 mL concentrated HNO_3 to 500 mL reagent water. Cap and shake to mix well.

7.7. Sulfuric acid / nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

7.8. SPLP Leaching fluids

7.8.1. SPLP solutions are unbuffered and exact pH may not be attained. The pH of TCLP and SPLP fluids should be checked prior to use. If not within specifications, the fluid should be discarded and fresh fluid prepared.

7.8.2. SPLP fluid #1: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 4.20 ± 0.05 This fluid is used for soils from a site that is east of the Mississippi River and for wastes and wastewaters.

7.8.3. SPLP fluid #2: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 5.00 ± 0.05. This fluid is used for soils from a site that is west of the Mississippi River.

7.8.4. SPLP fluid #3: This fluid is reagent water and is used for leaching of volatiles. Additionally, any cyanide-containing waste or soil is leached with fluid #3 because leaching of cyanide containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.9. Methanol and methylene chloride - used to aid in cleaning oil contaminated equipment.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples being analyzed for non-volatile organic compounds should be collected and stored in glass containers with Teflon lid liners. Chemical preservatives shall NOT be added UNTIL AFTER leachate generation.

8.2. Samples being analyzed for metals only can be collected in either glass or polyethylene containers.

8.3. When the waste is to be evaluated for volatile analytes, care should be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon lined septum capped vials with minimal headspace and stored at $4 \pm 2°C$). Samples should be opened only immediately prior to extraction.

8.4. Samples should be refrigerated to 4 ± 2°C unless refrigeration results in irreversible physical changes to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

8.5. The minimum TCLP sample collection size is determined by the physical state or states of the waste and the analytes of concern. The amount of waste required varies with the percent solids. The lower the percent solids, the more waste will be required for preliminary and final testing. For aqueous samples containing between 0.5 and 10% solids, several kilograms of sample are required to complete the analyses. The general minimal requirements when the samples are 100% solids include: 1 - 32 oz jar for semi-volatile organic analysis and metals, and 1 - 4 oz jar for volatile organic analysis. Low density sample materials, such as rags or vegetation, will require larger volumes of sample. For liquid samples (less than 50% solids), minimum requirements are 2 - 32 oz jars for semi-volatile organic analysis and metals, and 2 - 8 oz jars for volatile organic analysis. If volatile organic analysis is the only requested parameter, 2 separate jars are required. If matrix spike or duplicate control samples are requested, additional sample volume is required. If sufficient sample volumes were not received, analyses cannot be started and the client should be notified as soon as possible.

8.6. TCLP leachates should be prepared for analysis and analyzed as soon as possible following extraction. Leachates or portions of leachates for metallic analyte determinations must be acidified with nitric acid to a pH less than 2, unless precipitation occurs. If precipitation occurs upon addition of nitric acid to a small aliquot of the leachate, then the remaining portion of the leachate shall not be acidified and the leachate shall be analyzed as soon as possible. All other leachates should be stored under refrigeration (4 ± 2°C) until analyzed. ZHE leachates must be stored in VOA vials filled to eliminate all headspace.

8.7. Samples are subject to appropriate treatment within the following time periods:

Table 1 – Holding Times (days)

Parameter	Collection to Start of TCLP Leach	End of TCLP Tumble to Preparation	Start of TCLP Leach or Semi- volatile Prep Extraction to Analysis	Total Elapsed Time
Volatiles:	14	N/A	14	28
Semi-volatiles:	14	7	40	61
Mercury:	28	N/A	28	56
Other Metals:	180	N/A	180	360

NOTE: The initial holding time is measured from date of collection to date TCLP extraction started. (This should be the TCLP extraction date in QuanTims.) Semi-volatile method prep holding time is measured from the day tumbling is complete

to the start of method extraction Subsequent analysis holding times are measured from the date extraction (TCLP or method prep) starts. If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding holding times is not acceptable in establishing that a waste does not exceed the regulatory level Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory limit. The Total Elapsed Time is to be used as guidance. If preps are initiated at the last possible moment of a holding time, the elapsed times may be exceeded.

9. QUALITY CONTROL

9.1. Quality Control Batch (QC Batch) - QA-003 defines a QC Batch as a set of up to 20 field samples of similar matrix that behave similarly and are processed using the same procedures, reagents and standards within the same time period. The same lot of reagents must be used within a batch. A minimum of one TCLP extraction blank (Method Blank), one Laboratory Control Sample (LCS), one Matrix Spike (MS), and one Matrix Spike Duplicate (MSD) will be prepared with each TCLP leachate batch.

9.2. TCLP Extraction Blanks - A minimum of one blank (using the same extraction fluid as used for the samples) must be prepared and analyzed for every batch of samples extracted in a particular vessel type. The blanks are generated in the same way as the samples (i.e., blanks will be tumbled and filtered with the samples). ZHE Extraction vessels will be uniquely numbered. Consult the STL QC Program and the individual analysis SOPs for blank acceptance criteria.

9.3. Laboratory Control Sample (LCS) - A LCS is required with each batch of 20 or fewer samples. The LCS shall be generated after a batch of TCLP leachates have been generated (i.e., at the time of the preparative digestion or extraction) by spiking an aliquot of the appropriate extraction fluid used for that batch or reagent water. Consult the individual analysis SOPs for additional LCS guidance (i.e., spike amounts, spike levels, recovery criteria, etc.).

9.4. Matrix Spike (MS/MSD) - Matrix spikes are used to monitor the performance of the analytical methods on the matrix and to assess the presence of interferences. A MS/MSD pair are required with each batch of 20 or fewer samples.

9.4.1. Matrix spikes are to be added after filtration of the TCLP leachate. Spikes are not to be added prior to the TCLP leaching. For metals, matrix spikes are to be added before preservation with nitric acid.

9.4.2. Consult the individual analysis SOPs for additional guidance on spike compounds and levels.

9.5. Corrective Actions

9.5.1. Consult the STL QC Program and individual analysis SOPs for corrective action for blanks and LCS

9.5.2. Method of Standard Additions (MSA) shall be used for metals if all of the following conditions are met:

- Recovery of the analyte in matrix spike is not at least 50%,
- the concentration of the analyte does not exceed the regulatory level, and
- the concentration of the analyte measured in the sample is within 20% of the appropriate regulatory level.

If the matrix spike recovery is 5% or less due to dilution or matrix interference, contact the project manager and client for guidance. The client should also be contacted prior to initiation of any MSA steps. Refer to the individual analysis SOPs for details on how to perform MSA analysis.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to appropriate analysis SOPs.

11. PROCEDURE

11.1. GENERAL COMMENTS

11.1.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented on a Nonconformance Memo kept in the project file and described in the final report. The variation must be approved by a project manager, Technical Specialist and QA Manager. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.1.2. All masses should be recorded to the nearest 0.1 g.

11.2. PRELIMINARY SAMPLE EVALUATIONS (Refer to Flow Chart #1, Appendix D)

11.2.1. Determine the total volume of TCLP leachate (solid phase leachate + liquid filtrate) that needs to be generated for analysis according to the following:

Table 2. Recommended TCLP Leachate Volume

Analysis	TCLP Required Volume (mL)	SPLP Required Volume (mL)
Volatiles	3 x 40	3 x 40
Semi-volatiles	500	1000
Pesticides	500	1000
Herbicides	500	1000
Metals	300	300

11.2.1.1. For TCLP and SPLP samples used for matrix spike and matrix spike duplicate analysis, two to three times the listed volumes are required.

11.2.2. Sample Description (determine sample matrix)

11.2.2.1. Solid - If the waste will obviously yield no free liquid when subjected to pressure filtration , then proceed to Section 11.2.5 or 11.4 (Bottle Extraction Procedure or ZHE Procedure).

11.2.2.2. Liquid - If the sample is a monophasic liquid, proceed to Section 11.2.3 (Percent Solid Determination).

11.2.2.3. Multiphasic – The sample has discernible layers (liquid/liquid or liquid/solid). If more than one container of multi-phasic materials is received from the field, each container might show different amounts of each phase. Consult client to determine sample selection alternatives (composite all sample containers, select one, resample, etc.) if this occurs.

11.2.3. Solids Determination

11.2.3.1. Determine Type of Filtration Apparatus and Process

11.2.3.1.1. Percent Solids and ZHE Extractions - The ZHE filtration apparatus cannot accurately determine percent solids less than 5%. If an extraction is to be performed solely for volatile organic

compounds and the percent solids concentration is apparently greater than 5%, proceed to Section 11.4 (ZHE Extraction Procedure, Volatile Constituents). Otherwise, continue with Section 11.2.3.2. The aliquot of sample used here cannot be used again for the ZHE extraction.

11.2.3.1.2.If the sample is mostly a non-viscous liquid (water or non-viscous organic liquid) of low solids content (expected to be < 0.5%) , vacuum filtration should be used initially. Proceed to determination of percent dry solids (Section 11.2.3.2)

11.2.3.1.3.If the sample is viscous (sludge, oil, or is expected to have solids content > 0.5%), use pressure filtration. Proceed to determination of wet solids (Section 11.2.3.3).

11.2.3.2.Determination of percent dry solids

11.2.3.2.1.Measure and record the weight of the filter. Load the filter into the filter holder and assemble vacuum filter apparatus.

11.2.3.2.2.Homogenize the waste, then transfer 100 g subsample to a glass beaker. Record the sample weight in the percent dry solids section of the logbook.

11.2.3.2.3.Turn on vacuum source. Transfer the sample to the vacuum filtration device attempting to spread the waste sample evenly over the surface of the filter. Be sure to transfer all particulates from the beaker to the filter. Use a reagent water rinse if necessary.

11.2.3.2.4.Once all liquid has been pulled though the filter, remove the filter with the wet solids from the vacuum filtration apparatus.

11.2.3.2.5.Dry the filter and solid phase at 100 ± 20 ° C for approximately 15 minutes.

11.2.3.2.6.Remove the filter from the oven and allow to cool in a desiccator.

11.2.3.2.7.Weigh and record the dry weight of filter + particulates.

11.2.3.2.8.Calculate and record the percent dry solids.

11.2.3.2.9. If the percent dry solids is ≥ 0.5%, repeat the drying step. Weigh and record the second filter + particulates dry weight. If the two weighings do not agree within 1%, perform additional drying and weighing until successive weighings agree within 1%.

11.2.3.2.10. If the dry solids result is ≥ 0.5%, proceed to Section 11.2.3.3 using a fresh wet portion of the multiphase waste.

11.2.3.2.11. If the percent solids result is less than 0.5%, discard the solid phase. No leaching will be necessary. Filter sufficient sample with either the pressure filtration system or ZHE system as described in Sections 11.3 and 11.4. The filtrate is the TCLP leachate.

11.2.3.3. Determination of wet solids

11.2.3.3.1. Assemble the pressure filtration apparatus (use blunt forceps to handle the 0.6 to 0.8 μm filter membrane).

11.2.3.3.2. Homogenize the waste, transfer a minimum of a 100 mL subsample to the glass beaker. Measure and record the gross weight (logbook column A).

11.2.3.3.3. Measure and record the tare weight of the filtrate collection bottle (logbook column D).

11.2.3.3.4. Transfer the sample to the filtration device attempting to spread the waste sample evenly over the surface of the filter. Measure and record the tare weight of the empty glass beaker and any residual sample (logbook column B).

11.2.3.3.5. Calculate and record the net weight of sample used for testing (logbook column C).

11.2.3.3.6. Slowly apply gentle pressure of 10 psi to the filtration apparatus. Allow the sample to filter until no SIGNIFICANT additional liquid has passed through the filter during a 2 minute period.

11.2.3.3.7. If necessary, repeat previous step by increasing the pressure in 10 psi increments until a maximum of 50 psi is reached. Stop the filtration when no additional filtrate is generated within a 2 minute period.

Note: Some samples will contain liquid material that does not filter (e.g., oil). Do not attempt to filter the sample again by exchanging filters. Viscous oils or any wastes which do not pass through the filter are classified by the method as a solid.

11.2.3.3.8. Remove the filtrate collection bottle, weigh and record the gross weight (logbook column E).

11.2.3.3.9. Calculate and record the net weight of filtrate (logbook column F). This result will be used in the percent solids calculation.

11.2.3.3.10. Pour the filtrate into an appropriately sized graduated cylinder. Measure and record the volume of the filtrate in the logbook.

11.2.3.3.11. Retain the filtrate for possible recombination with the leachate in Section 11.3.6. Retain the filter and wet solids for the leaching in Section 11.3.

11.2.3.3.12. For multiphase sample preparations, calculate the total weight of wet solids and record the result in logbook column G.

11.2.4. Particle-size Reduction for Fluid Selection

11.2.4.1. The subsample used for fluid selection must consist of particles less than approximately 1 mm in diameter (versus the less than 1 cm requirement for the material used for the actual extraction). The method requires a smaller particle size to partially compensate for the shorter duration of contact time with the leachate solution as compared to the full extraction. Inappropriate use of coarser materials could result in the selection of the wrong fluid type.

11.2.4.2. Surface area exclusion - size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram.

11.2.4.3. If the sample contains particles greater than approximately 1 mm in diameter, crush, cut, or grind the solids to the required size.

11.2.4.4. Consult a supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick).

11.2.5. Determination of Appropriate Extraction Fluid

11.2.5.1.If the solid content is greater than or equal to 0.5%, and if the sample is being analyzed for metals or nonvolatile organic compounds, the type of leaching solution must be determined.

11.2.5.2.Follow times, temperature, and particle size specified in this section as closely as possible. If reaction time between the acid solution and solid waste is too short or too long, the procedure may produce false pH readings.

11.2.5.3.For SPLP, refer to Section 7.8 for fluid selection. Record the fluid type in the logbook.

11.2.5.4.The TCLP leaching fluid for all volatiles is TCLP Fluid #1.

11.2.5.5.TCLP leach fluid determination for non-volatile analytes

11.2.5.5.1.Calibrate the pH meter with fresh buffer solution in accordance with the pH SOP.

11.2.5.5.2.Weigh out a 5.0 ± 0.1 g subsample (less than 1 mm particle size) of the solid phase into a glass container, and record in the logbook. Note: If sample quantity is limited, consult supervisor or manager.

Note: Many multiphase samples have limited solids quantity . In these instances use a 5 g aliquot of the whole sample. Document this difference in the logbook comment section.

11.2.5.5.3.Add 96.5 ± 1.0 mL of reagent water, cover with a watchglass, and stir for 5 minutes.

11.2.5.5.4.Measure and record the pre-test sample pH in the logbook.

Note: To avoid damaging a glass pH probe when organic liquid is present, use narrow range pH indicator paper or an ISFET pH meter.

11.2.5.5.5.If the pH is less than or equal to 5.0, use TCLP Fluid #1.

11.2.5.5.6.If the fluid pH is greater than 5.0, add 3.5 mL 1 N HCl. Slurry the sample briefly. Clip thermometer to the inside edge of one sample in each pre-test sample group to monitor the temperature.

All samples in the group must go on the hot plate at the same time in order for the temperature of the one monitored sample to represent the others. Heat to 50°C and maintain for 10 minutes.

Note: The heating cycle is a critical step. If the solid waste does not remain in contact with the acidic solution under specified time and temperature conditions, an erroneous pH may be measured.

11.2.5.5.7. Cool to room temperature.

11.2.5.5.8. Measure and record the pH immediately after the sample has reached room temperature.

11.2.5.5.8.1. If the pH is less than or equal to 5.0, use TCLP Fluid #1. Record the buffer in the logbook.

11.2.5.5.8.2. If the pH is greater than 5.0, use TCLP Fluid #2. Record the buffer in the logbook.

11.2.6. For samples requiring analysis for semi-volatile organics, pesticides, herbicides or metals proceed to Section 11.3.

11.2.7. For samples requiring analysis for volatile organics (ZHE), proceed to Section 11.4.

11.3. BOTTLE EXTRACTION PROCEDURE: NON-VOLATILE CONSTITUENTS: SEMI-VOLATILES, PESTICIDES, HERBICIDES, METALS (Refer to Flow Chart #2, Appendix D)

11.3.1. Evaluate the solid portion of the waste for particle size. If it contains particles greater than 1 cm in size, prepare the solid portion of the waste for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size (i.e., capable of passing through a 9.5 mm, 0.375 inch, standard sieve). Size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram. If particle size reduction was required, record this in comments column in logbook.

11.3.1.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Determination of particle size reduction tools should take into account the requested analytes (e.g. avoid chromium steel tools when TCLP metals have been requested). Bricks, rocks, or other solids amenable to grinding may be

subcontracted out for particle size reduction. (Contact PA or PM.) Note that size reduction to fine powder is not appropriate, and could invalidate results. If necessary, consult client for guidance.

11.3.2. Determine the minimum total volume of solid phase leachate that needs to be generated. Refer to Section 11.2.1.

11.3.3. Use 100 g of solid unless sample quantity is limited. If limited sample, divide the total volume of solid phase leachate required by 20 to determine the minimum mass of solid phase required for leaching. Round this mass UP to the nearest 5g. Client must be notified if less than 100 g of solid material is used.

Note: Solid phase material is often in limited quantity from multiphase samples. Generally all the *solid* phase material and the filter from Section 11.2.3.3.11 are transferred to the leaching bottle

11.3.4. Weigh the required mass of solid phase into an appropriate bottle (plastic for metals only, glass for all others) and **slowly** add 20 times its mass of appropriate leaching fluid (e.g., 100 g of sample would require 2000 mL of leaching fluid). Record the weight of the sample aliquoted for the extraction. Record the volume of extraction fluid added in the logbook if other than 2000 mL.

11.3.5. Ensure any effervescence has stopped before capping the bottle tightly. Secure in a rotary agitator and rotate end-over-end at 28-32 rpm for 16-20 hours. The temperature of the room should be 23 ± 2°C. Record the rotary agitator I.D. and the date and time extraction is started and completed in the logbook.

NOTE: As agitation continues, pressure may build up within the bottle for some types of wastes. To relieve excessive pressure, the bottle may be removed and opened periodically in a properly vented hood to relieve any built-up pressure

11.3.6. After tumbling in the rotary agitator is completed, remove the bottle and allow the solids to settle. Record the date and time the extraction is completed in the logbook. If sample was multiphase with an initial filtrate, drop a few drops of the filtrate (with a disposable glass pipette) into the extraction bottle and observe whether the filtrate is insoluble or forms a precipitate with the leachate. If so then the filtrate is not compatible with the leachate and must be bottled and analyzed separately. The results are normally mathematically recombined (Section 12.1.2). If the filtrate is compatible with the leachate (ie completely soluble) then pour the entire filtrate into the leachate bottle, recap and mix. Proceed with the leachate filtration step in the next section.

11.3.7. Filter the sample using pressure filtration by filtering through a new glass fiber filter. For final filtration of the TCLP leachate, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filters must be acid washed if metals are to be determined (see Section 6.3). The entire sample need not be filtered; however, sufficient volume should be generated to support the required analyses.

11.3.8. Measure the pH of the TCLP leachate and record in the logbook. (Use narrow range pH paper or ISFET pH meter to measure the pH of oily samples as a glass pH probe may be damaged .)

11.3.9. Prepare subsamples for metals for MS/MSD quality control testing using the appropriate TCLP spiking solution (do not spike for organics). Refer to the appropriate determinative SOPs for further guidance on the spike components, levels and action criteria.

11.3.10. Immediately preserve the leachate as follows:

Metals	pH < 2 w/ HNO_3 for aqueous filtrates and leachates (do not acidify oils and other non-aqueous liquids)
All others	Refrigerate to 4 ± 2 °C

Note: Refer to Section 8.6 if precipitation occurs upon preservation.

11.3.11. Label each sample with the appropriate information and submit to the appropriate analytical groups for prep and analysis. For multiphase samples requiring mathematical recombination provide copies of the TCLP preparation logbook sheets to the sample preparation and analysis groups. Most mathematically recombined samples will require data entry for the filtrate and leachate portions as well as for the mathematically recombined results. Contact the project manager to ensure the proper sample login is completed.

11.4. **ZHE EXTRACTION PROCEDURE: VOLATILE CONSTITUENTS** (Refer to Flow Chart #3, Appendix D)

11.4.1. Use the ZHE device to obtain a TCLP leachate for analysis of volatile compounds only. Leachate resulting from the use of the ZHE shall NOT be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, herbicides and semi-volatile organics).

11.4.2. Due to some shortcomings of the method, losses of volatile compounds may occur. Extra care should be observed during the ZHE procedure to ensure that such losses

are minimized. Charge the ZHE with sample only once and do not open the device until the final extract has been collected. Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere any longer than necessary.

11.4.3. Install new O-rings and adjust the ZHE piston in the ZHE body to the appropriate height (slightly moisten the O-rings with leaching fluid if necessary).

11.4.4. If the preliminary evaluations indicated the need for particle size reduction, homogenize the waste, weigh out a sufficient size subsample and prepare for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size as measured with a ruler (Do NOT sieve the sample). Size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram If particle size reduction was required record this in the comments column of the logbook.

Note: To minimize loss of volatiles, samples for volatiles that require particle size reduction should be kept in sample storage (at 4°C) until immediately before size reduction. Aggressive reduction which would generate heat should be avoided and exposure of the waste to the atmosphere should be avoided to the extent possible. Size reduction to a fine powder is not appropriate. Also see Section 11.3.1.

11.4.4.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Bricks, rocks, or other solids amenable to grinding may be subcontracted out for particle size reduction (Contact PM).

11.4.5. Homogenize and transfer an appropriate size subsample of the waste into the ZHE and record the mass in the logbook.

11.4.5.1. For wastes that are solid, a 15 g sample is used.

11.4.5.2. For wastes containing < 0.5% solids, the liquid portion of the waste, after filtration, is defined as the TCLP leachate. Filter enough of the sample to support all of the volatile analyses required.

11.4.5.3. If the sample has ≥ 0.5% solids and has non-volatile TCLP/SPLP requested, the appropriate sample size should be estimated based on the wet solids content determined in Section 11.2.3.3. If ZHE only, use visual wet solids estimate to sample subaliquot.

Note: For wastes containing greater than 0.5% wet or dry solids, the "solids" value from the ZHE filtration process may be used to determine the volume of fluid to load into the ZHE. This approach is recommended since the solids value from Section 11.2.3.3 may differ from the ZHE filtration solids due to sample variability or differences in the filtration apparatus.

11.4.6. Carefully place the glass fiber filter between the support screens and secure to the ZHE. Tighten all the fittings.

11.4.7. Place the ZHE in a vertical position; open both the gas AND liquid inlet/outlet valves. Attach a gas line to the gas inlet/outlet valve.

11.4.8. If the waste is solid, slowly increase the pressure to a maximum of 50 psi to force out as much headspace as possible and proceed to Section 11.4.13.

11.4.9. If this is a mutliphase sample, carefully apply gentle pressure of 10 psi (or more, if necessary) to force all headspace slowly out of the ZHE. At the FIRST appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue gas pressure.

11.4.10. Assemble a syringe and place the plunger in all the way. Attach the pre-weighed syringe to the liquid inlet/outlet valve and open the valve. Record the tare weight of the collection syringe in column D of the logbook. .

11.4.11. Carefully apply gas pressure of no more than 10 psi to force out the liquid phase. Allow the sample to filter until no SIGNIFICANT additional filtrate has passed in a 2 minute period.

Note: If the capacity of the syringe is reached, close the liquid inlet/outlet valve, discontinue gas pressure, remove the syringe, weigh, record weight in column E and filtrate volume in the logbook. Return to Section 11.4.10.

11.4.12. Repeat previous step increasing the pressure in 10 PSI increments until 50 psi is reached and no significant liquid has passed in a 2 minute period. Close the valve and discontinue gas pressure. Remove the collection device and record the total weight of the collection device with filtrate in column E and filtrate volume in the logbook. Transfer the filtrate to VOA vials and label appropriately. Calculate the weight of filtrate collected and record in column F in the logbook.

Notes: If the original waste contained less than 0.5% solids (Section 11.2.3.2), this

filtrate is defined as the TCLP leachate and you may proceed to Section 11.4.22. Otherwise, save the vials by storing at 4°C under minimal headspace conditions, for recombination as in Section 11.4.21.

The material remaining in the ZHE is defined to be the "solid" phase. Calculate the weight of the solid phase and record in column G of the logbook by subtracting the weight of the filtrate from the weight of the sample.

11.4.13. Determine the amount of buffer to use. Solid samples use 300 mL of leach fluid (20 X 15 g). For multiphase samples use the wet solids (column G) amount and multiply by 20. Record the leach fluid volume in column H of the logbook.

Note: The TCLP ZHE prep uses only TCLP fluid #1; the SPLP ZHE prep uses only SPLP fluid #3.

11.4.14. Load the fluid transfer reservoir with an excess of Fluid #1 and preflush the transfer line to eliminate air pockets. Be sure the required volume remains.

11.4.15. Attach the transfer line to the liquid inlet/outlet valve and open the valve. Carefully pump the required volume into the ZHE and close the valve. Disconnect the transfer line.

11.4.16. Check the ZHE to make sure all the valves are closed and manually rotate the ZHE (end-over-end) 2 or 3 times. Reposition the ZHE in the vertical position.

11.4.17. Pressurize the ZHE to 5-10 psi. If the ZHE appears to be leaking, follow the corrective action protocols recommended by the manufacturer and repeat the analysis.

11.4.18. Slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced during the introduction of the Fluid. Upon the first sign of liquid from the valve, close the valve.

11.4.19. Repressurize the ZHE to 5-10 psi and place in the rotary agitator. Rotate at 28-32 rpm for 16-20 hours. Room temperature should be 23 ± 2 °C. The room temperature is recorded using a continuous temperature monitor.

11.4.20. Confirm that the pressure of 5-10 psi was maintained throughout the leaching. If it was NOT maintained, return to Section 11.4 and repeat the leachate with a new aliquot of sample.

11.4.21. If there is an initial liquid filtrate (Sec 11.4.12) determine if it is compatible with the leachate if the filtrate has not been previously tested (Sec. 11.3.6).

11.4.21.1. Remove the plunger from the syringe and attach the barrel to the ZHE vessel. Open the outlet valve and pressurize as necessary to transfer about 1 mL of leachate into the syringe. Close the outlet valve.

11.4.21.2. With a glass pipette transfer a few drops of initial filtrate into the open syringe barrel. Formation of separate layers or a precipitate indicates the filtrate and leachate are not compatible. Bottle the filtrate for separate preparation and analysis. The results are normally mathematically recombined.

11.4.21.3. If the filtrate is compatible gently pour the remainder of the filtrate into the syringe barrel. Install the plunger. Bleed any pressure in the ZHE piston. Open the inlet/outlet valve and depress the syringe plunger to inject the filtrate into the ZHE vessel. Do not inject the air bubble (if present) from the syringe.

11.4.21.4. Close the valve and rotate a few times to mix. Proceed with leachate filtration as described in the next section.

11.4.22. Attach an empty syringe to the outlet valve. Open the valve and pressurize the piston to expel the leachate from the ZHE vessel. Following collection, store the TCLP leachate in 2 or 3 40-mL VOA vials with minimal headspace at 4 ± 2 °C and prepare for analysis as soon as possible using the appropriate organic analysis procedure (see Section 16.3).

11.4.23. If the individual phases are analyzed separately, combine the results mathematically by using the recombination calculation in Section 12.1.2. . Provide copies of the TCLP preparation logbook sheets to the sample preparation and analysis groups. Most mathematically recombined samples will require data entry for the filtrate and leachate portions as well as for the mathematically recombined results. Contact the project manager to ensure the proper sample login is completed.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

12.1.1. Calculation of weight of extraction fluid to use:

Volume of extraction fluid = 20 X weight of wet solids to be extracted

12.1.2. Mathematical recombination of analytical results:

$$Final\ Analyte\ Concentration = \frac{(V_1 \times C_1) + (V_2 \times C_2)}{V_1 + V_2}$$

V_1 = total volume of the initial filtrate phase (L).
C_1 = analyte concentration in initial filtrate phase (mg/L).
V_2 = volume of the theoretical solid phase leachate (L).
C_2 = analyte concentration in solid phase leachate (mg/L).,

12.2. REPORTING REQUIREMENTS

12.2.1. Follow these reporting conventions for multi-phase samples:

12.2.1.1. If both phases have positive results, use the values from each phase to calculate the recombined result. Use the reporting limit for each phase to calculate the recombined reporting limit.

12.2.1.2. If both phases are "ND" (not detected) the recombined result is "ND," and the reporting limit is calculated from the reporting limit for each phase.

12.2.1.3. If one phase is "ND" and the other phase has a positive result, use the zero for the "ND" phase and the positive value for the other phase to calculate the combined result. This will produce a minimum known concentration. Alternatively, at client request, the maximum possible concentration can be calculated by using the reporting limit for the "ND" phase rather than zero. The combined reporting limit is based on the reporting limit for both phases

12.2.2. Units - regardless of the nature of the sample, all TCLP and SPLP results are reported in units of mg/L.

12.2.3. For limits and significant figures, consult the appropriate analytical methods (Section 16.3).

12.2.4. Anomalies - all anomalies observed during the leach procedure must be noted on the worksheet or an NCM form. Some examples of such anomalies are:

12.2.4.1. Sample was monolithic - particle size reduction not possible due to nature of matrix.

12.2.4.2. Insufficient sample - less than the required 100 g minimum was available.

12.3. REVIEW REQUIREMENTS

12.3.1. Review all applicable holding times. If a holding time was exceeded, confirm that a holding time violation was properly documented in an NCM.

12.3.2. If Total analysis results are available, those results may be compared with the TCLP analysis results according to the following:

$$Total \geq 20 \times TCLP$$

NOTE: Assumes the sample is 100% Solids.

12.3.3. Total constituent analysis results can be used to demonstrate the TCLP protocol is unnecessary. In performing a TCLP analysis, there is a 20:1 dilution of the original sample with the leaching solution. Thus, if the "total constituent" result is less than 20 times the TC level, it is impossible for the leachate to "fail" and the TCLP does not need to be performed. For example, the TC level for lead is 5.0 mg/L (ppm). Therefore, if a sample of lead-contaminated soil contains less than 100 ppm total lead, a TCLP test need not be run to demonstrate that lead is less than the TCLP limit.

13. METHOD PERFORMANCE

13.1. Refer to individual analysis SOPs.

13.2. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure must be segregated and disposed according to the facility's hazardous wastes procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Method 1311, Toxicity Characteristic Leaching Procedure, Revision 0, July 1992, SW-846 Final Update I.

16.2. Method 1312, Synthetic Precipitation Leaching Procedure, Revision 0, November 1994, SW-846 Update II.

16.3. Related Documents

16.3.1. Toxicity Characteristic: Corrections to Final Rule. Method 1311, Federal Register, Vol. 55, No. 126, Friday, June 29, 1990.

16.3.2. Toxicity Characteristic: Final Rule. Method 1311, Federal Register, Vol. 55, No. 61, Thursday, March 29, 1990.

16.3.3. Technical Background Document and Response To Comments, Method 1311, Toxicity Characteristic Leaching Procedure, USEPA/OSW, April, 1989.

16.3.4. QA-003, Quality Control Program

16.3.5. CORP-IP-0003NC: Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods.

16.3.6. CORP-MT-0001NC: Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis, Method 6010B and Method 200.7.

16.3.7. CORP-MT-0003NC: Graphite Furnace Atomic Absorption Spectroscopy, (Thallium only)

16.3.8. CORP-MT-0005NC: Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1.

16.3.9. CORP-MS-0002NC: Determination of Volatile Organics by GC/MS based on Methods 8260B, 624, and 524.2.

16.3.10.CORP-MS-0001NC : GC/MS Analysis Based on Method 8270C and 625.

16.3.11. CORP-GC-0001NC: Gas Chromatographic Analysis Based on Methods 8000B, 8021B, 8081A, 8082, 8151A, 8310, 610, and 8141A.

16.3.12.CORP-OP-0001NC: Extraction and Cleanup of Organic Compounds from Waters and Soils, Based on SW846 3500 Series, 3600 Series, 8151A and 600 Series Methods.

17. MISCELLANEOUS

17.1. Modifications/Interpretations from Reference Methods

17.1.1. Section 11.2: Preliminary Evaluations. Section 7.1 of the source method 1311 states that the sample aliquot used for the preliminary evaluation "...may not actually undergo TCLP extraction." Section 7.1.5 of the source method indicates that the portion used for the preliminary evaluation may be used for either the ZHE or non-volatile extraction if the sample was 100% solid. Section 7.1.5 further indicates that if the sample was subjected to filtration (i.e., < 100% solid) that this aliquot may be used for the non-volatile extraction procedure only as long as sufficient sample is available (minimum 100 g). Samples which have been subjected to the oven drying step may not be used for TCLP extraction because solid phase degradation may result upon heating.

17.1.2. Sections 11.3.6 and 11.4.21: Determination of Filtrate/Extraction Fluid Compatibility. Section 7.2.13 of the source method provides no guidance as to how to make this determination. As a result, the procedure herein was developed.

17.1.3. Section 9.2: TCLP Extraction Blanks. Section 8.1 of the source method states that a minimum of one blank for every 20 extractions "...that have been conducted in an extraction vessel." STL has interpreted this to mean one blank per twenty samples leached per TYPE of leaching vessel (i.e., Bottle or ZHE) per leach fluid used.

17.1.4. Section 11.2.5.5.8.1: Determination of Appropriate Extraction Fluid. Method 1311 does not address the appropriate approach to take if the pH equals 5.0. This SOP requires that Fluid #1 must be used if the pH is less than or equal to 5.0.

17.1.5. Section 9.4: QA/QC - Matrix Spikes. Section 8.2 of the source method states "A matrix spike shall be performed for each waste type..." and "A minimum of one matrix spike must be analyzed for each analytical batch." Further, Section 8.2.3 of the source method also states "The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist." The standard STL LQM is designed to address the performance monitoring of analytical methodology through the LCS program. A minimum of one MS and MSD will be prepared for each TCLP leachate batch. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, the MS/MSD results have immediate bearing only on the specific sample spiked and not all samples in the batch.

17.1.6. Section 8.2.2 of the source method states that "In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level." The method also states "If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration but may not be less than five times the method detection limit". For several analytes, spiking at the regulatory level is inappropriate to the range of analysis afforded by the determinative methods. Due to the wide range in these levels, STL spikes at the levels specified in the determinative SOPs.

17.2. Modifications from Previous SOP

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

APPENDIX A

TABLES

Table 3 - Toxicity Characteristic Analytes and Regulatory Levels (Final Rule)

APPENDIX A - TABLES

Contaminant	mg/L
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresols	200.0
m-Cresols	200.0
p-Cresols	200.0
Total Cresols (used if isomers not resolved)	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
2,4-Dinitrotoluene	0.13
1,1-Dichloroethylene	0.7
Endrin	0.02
Heptachlor (& epoxide)	0.008
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1 0
Vinyl chloride	0.2

APPENDIX B

FIGURES

Figure 1 & 2 - Rotary Agitation Apparatus and Zero Headspace Extraction Vessel (ZHE)

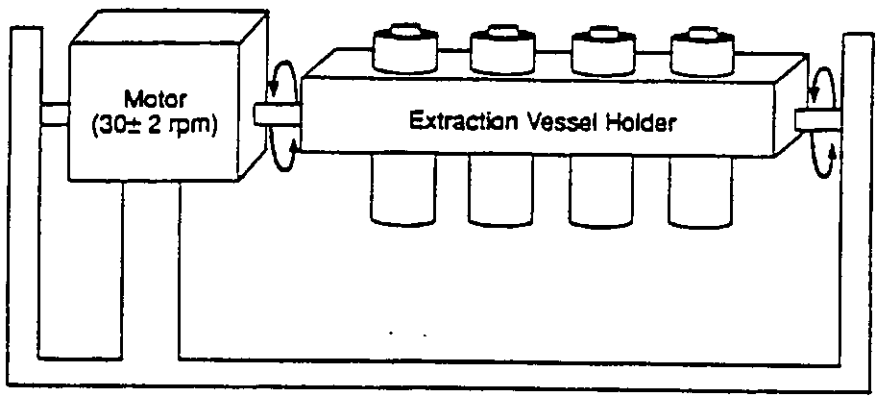

Figure 1. Rotary Agitation Apparatus

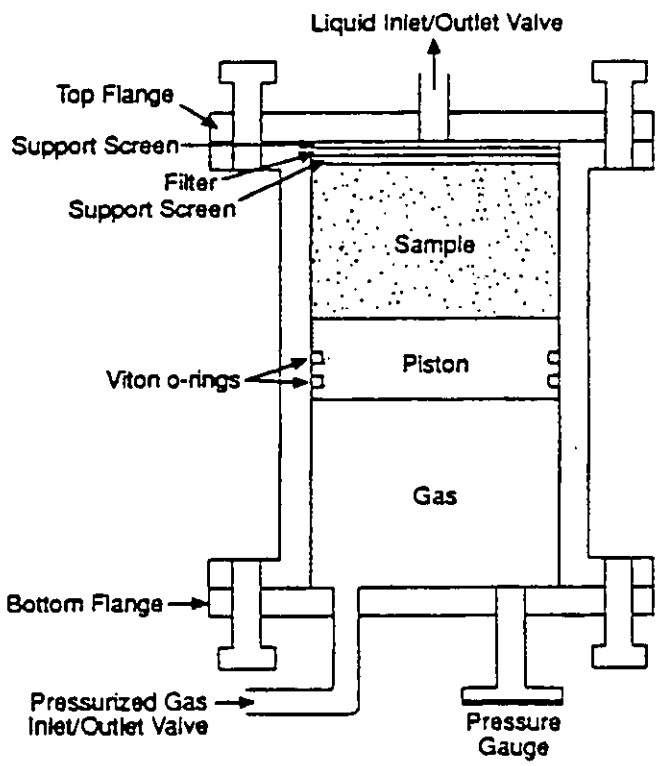

Figure 3 - US Environmental Protection Agency Memorandum #35, Page 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
SOLID WASTE AND EMERGENCY RESPONSE

MEMORANDUM # 35

DATE: June 12, 1992

SUBJECT: Notes on RCRA Methods and QA Activities

From: Gail Hansen, Chief
Methods Section (OS-331)

This memo addresses the following topics:

- o 1992 Symposium on Waste Testing and Quality Assurance
- o SW-846 Update
  - Final Rule for January 23, 1989 Proposed Rule
  - Notice, Proposed Rulemaking for the Second Update to the Third Edition
- o Chlorofluorocarbon 113 (CFC-113) Solvent Replacement Update
- o Environmental Monitoring Methods Index (EMMI)
- o Sampling Work Group Formation
- o MICE Update
- o Oily Waste Analysis
- o Electronic SW-846 Availability.

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Figure 3 - US Environmental Protection Agency Memorandum #35, Page 10

Oily Waste Analysis

One of the most frequently asked questions on the MICE Service concerns the application of the TCLP, Method 1311, to oily wastes. Many callers request technical guidance on the extraction of oily wastes due to the difficulty in the filtration on these types of waste. In many cases, an oily waste does not filter completely due to premature clogging of the glass fiber filter. This can result in the retention of standing liquid on the glass fiber filter. Material that do not pass through the glass fiber filter at the conclusion of the filtration step is defined by the method as the solid phase of the waste. The solid phase is then subjected to the leaching procedure of the TCLP. For oily wastes, clogging of the glass fiber filter can result in an overestimation of the amount of solid material available for leaching.

To solve this problem, the Agency recommends a conservative approach, one that probably will overestimate the amount of leaching. Rather than performing the TCLP extraction on the unfiltered portion of the oily waste, assume the waste is 100% liquid (e.g., will pass through the glass fiber filter) and perform a totals analysis on the oily waste to determine if the oil exceeds the appropriate regulatory level.

Filterable waste oil generated during the TCLP must be analyzed for a variety of organic and inorganic analytes. The OSW recognizes the difficulty in achieving acceptable performance for the analysis of waste oil using methods currently provided in SW-846. As a result, the Agency will provide several new methods for the preparation and analysis of oil samples to the Organic Methods Workgroup in July. In addition, a microwave assisted digestion procedure should improve the analysis of metals and will be proposed as part of the Second Update of the Third Edition of SW-846. Brief descriptions of these techniques are provided below, for additional information on the organic procedures contact Barry Lesnik at (202) 260-7459. For additional information on microwave digestion contact Ollie Fordham (202) 260-4778.

The use of purge-and-trap (Method 5030) for volatiles in oil generally results in severe contamination of analytical instrumentation. Traps, transfer lines and chromatography columns may become contaminated with oil. This leads to elevated baselines, hydrocarbon background in subsequent analyses, and cross-contamination. Headspace (Method 3810) is currently allowed only as a screening procedure in SW-846. The Agency is evaluating the use of headspace in conjunction with isotope dilution mass spectrometry for the quantitative analysis of volatiles in oil. Headspace reduces interference problems encountered with purge-and-trap. However, headspace quantitation can be questionable because the distribution of analytes is not

APPENDIX C

Logbook Pages

TCLP/SPLP ZHE Logbook

STL NORTH CANTON ZHE LOGBOOK

Sample Number	Extraction Vessel ID	Matrix	Sample Wt (g)	Extraction Buffer ID	Date On	Time On	Date Off	Time Off	Tumbler ID	Tumbler Speed 30±2 rpm	Extraction Fluid ID	Initial ZHE Pressure	Final ZHE Pressure	Comments

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APPENDIX C – Logbook Pages

APPENDIX C – Logbook Pages

STL NORTH CANTON ZHE LOGBOOK

	A	B	C	D	E	F		G	H	
Sample Number	Weight of Container + Sample (g)	Weight of Container + Residue (g)	Difference (A – B) Sample Weight (g)	Weight of the Syringe (or vials) (g)	Weight of the Syringe (or vials) + Filtrate (g)	Difference (E – D) Filtrate Weight (g)	Volume of Filtrate* (mL)	Difference (C – F) Wet Solids Weight (g)	G x 20 Buffer Amount (mL)	Initials

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APPENDIX C – Logbook Pages

* Filtrate volume only needed when filtrate is incompatible with leachate

TCLP/SPLP Bottle Extraction Logbook

SOP No.: NC-IP-0005

STL NORTH CANTON TCLP LOGBOOK

				Pre-Test			% Dry Solids				Leach Start					Leach Finish					
Pre-Prep Batch	Sample Number	Parameters	Matrix	Sample Wt (g)	pH after water	pH after heating	Sample Wt (g)	Filter Wt (g)	Filter + Particulates Wt (g)	% Dry Solids	Sample Wt (g)	Buffer # / ID	Date On	Time On	pH On	Date Off	Time Off	pH Off	Tumbler ID	Initials	Comments
		M B P H																			
		M B P H																			
		M B P H																			
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APPENDIX C – Logbook Pages

APPENDIX C – Logbook Pages

SOP No.: NC-IP-0005 STL NORTH CANTON TCLP LOGBOOK

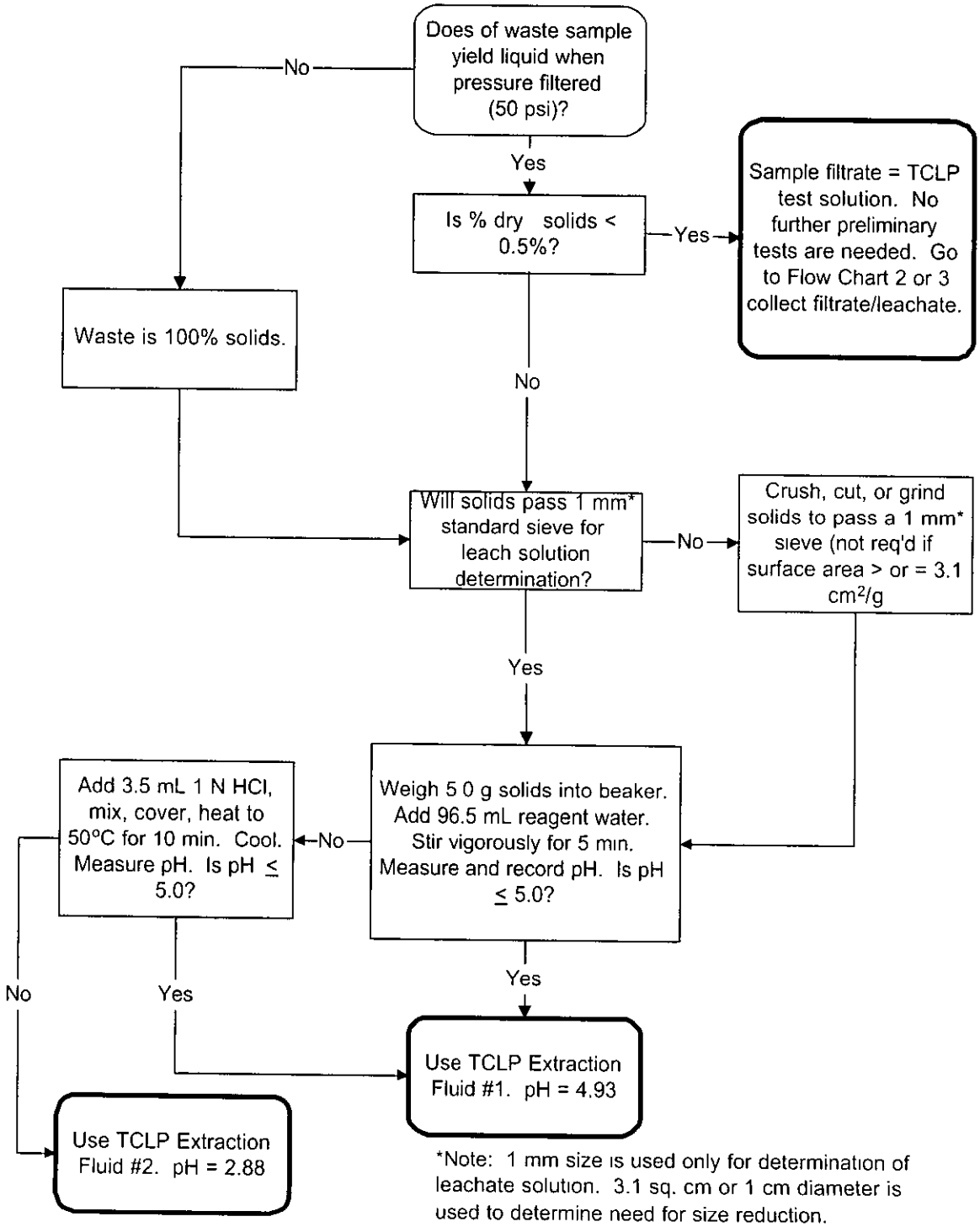
	A	B	C	D	E	F		G	H		
Sample Number	Weight of Container + Sample (g)	Weight of Container + Residue (g)	Difference (A – B) Sample Weight (g)	Weight of the Filtrate Bottle (g)	Weight of the Filtrate bottle + Filtrate(g)	Difference (E – D) Filtrate Weight (g)	Volume of Filtrate* (mL)	Difference (C – F) Wet Solids Weight (g)	G x 20 Buffer Amount (mL)	Initials	Comments

* Filtrate volume only needed when filtrate is incompatible with leachate

APPENDIX D

FLOW CHARTS

Flow Chart 1. Preliminary Sample Evaluation (Section 11.2)



*Note: 1 mm size is used only for determination of leachate solution. 3.1 sq. cm or 1 cm diameter is used to determine need for size reduction.

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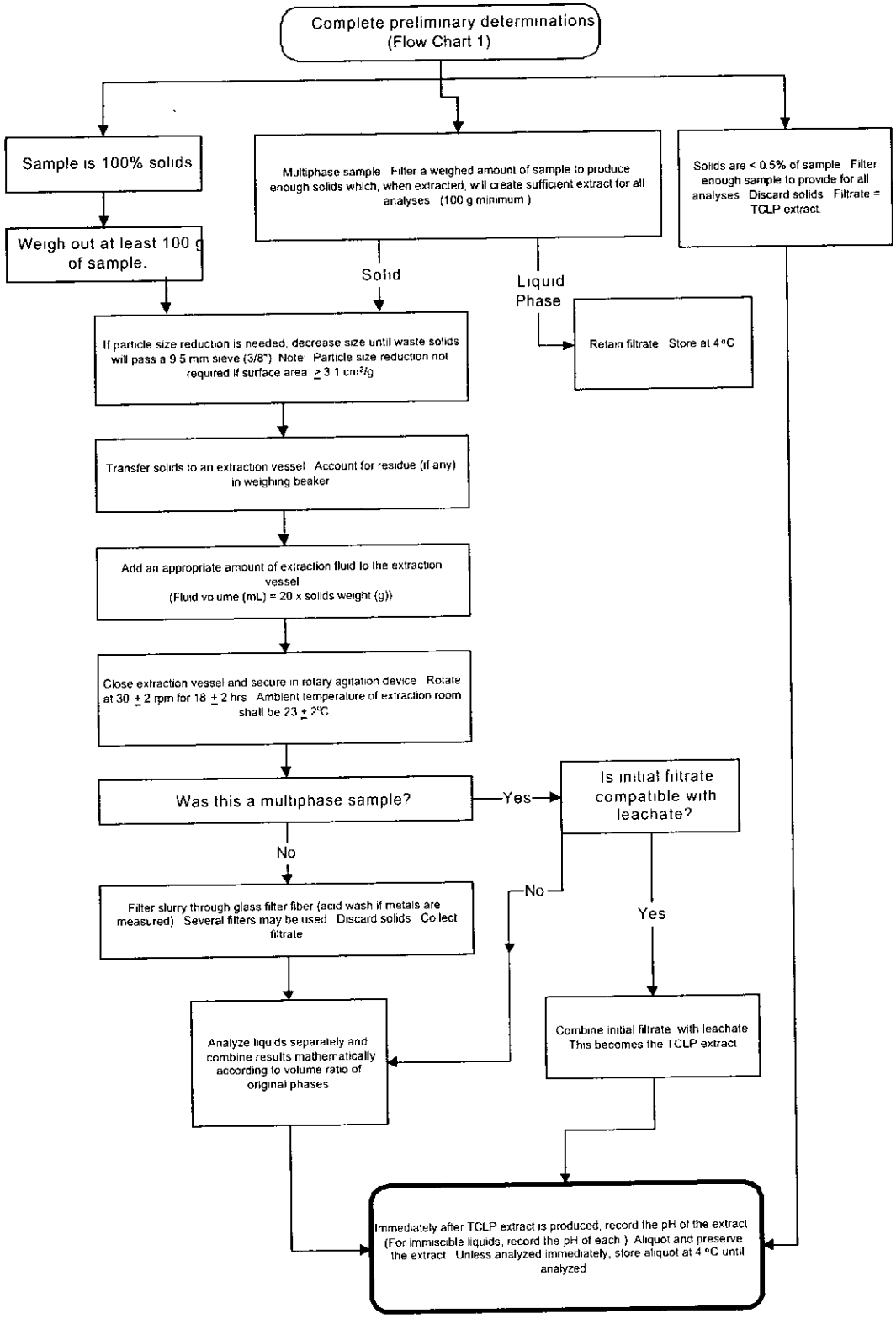
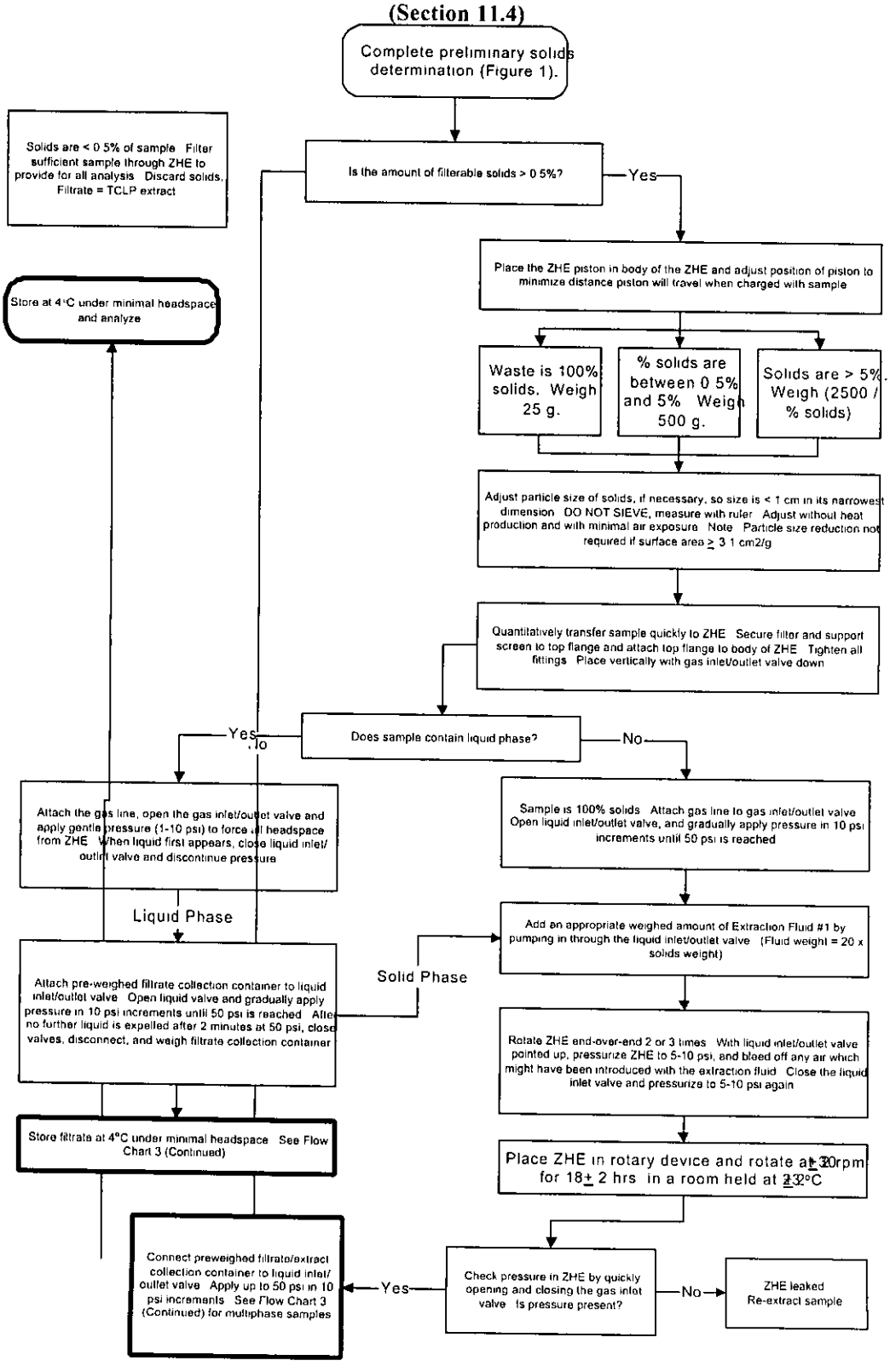
APPENDIX D - FLOW CHARTS

Flow Chart 2. Bottle Extraction, Non-Volatile Constituents (Section 11.3)

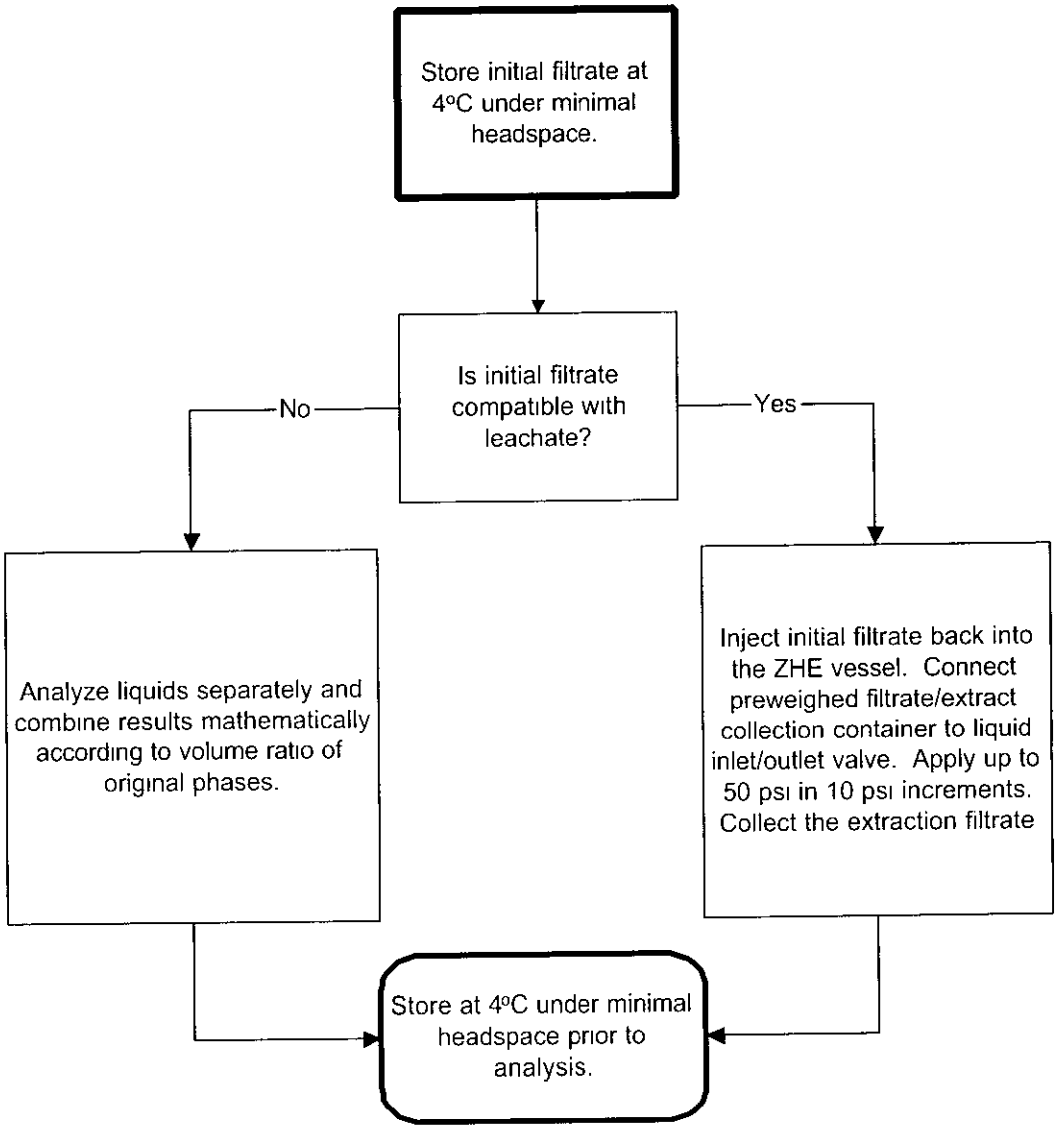


APPENDIX D - FLOW CHARTS

Flow Chart 3. ZHE Extraction, Volatile Constituents (Section 11.4)



Flow Chart 3. ZHE Extraction
(Continued)



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SOP No. NC-WC-0010
Revision No. 5
Revision Date: 02/05/03
Page 1 of 11

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PH ELECTROMETRIC METHOD

(SUPERSEDES: REVISION 4.1, DATED 11/28/00)

Prepared by: _____ 2/7/03
Date

Reviewed by: Angela Serra 2/7/03
Technology Specialist Date

Approved by: Beth Ramlet 2/10/03
Quality Assurance Manager Date

Approved by: Deborah Budd 2/7/03
Environmental Health and Safety Coordinator Date

Approved by: _____ 2/8/03
Laboratory Director Date

Proprietary Information Statement:

TABLE OF CONTENTS

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of pH in waters, wastewaters, and solids. It is based on SW846 Methods 9040B and 9045C and EPA Method 150.1. The approximate working range is 1 - 14 pH units. Samples with a pH of < 1 are reported as < 1.

1.2. The associated method codes are PU (9040B), OZ (9045C), and AJ (150.1). The preparation codes are 88 and 1C.

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. The pH is determined electrometrically by using an electrode. The pH meter is calibrated with a series of known pH buffers.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

4. INTERFERENCES

4.1. Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents {as well as glassware cleaning procedures that involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of an STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. pH meter with electrode(s) and temperature compensation

6.2. Beakers: various

6.3. Top loading balance: Capable of accurately weighing ±0.01 g

6.4. Stir plate and stir bars

6.5. Shaker or mechanical tumbler

6.6. Autotitrator

6.7. Centrifuges tubes

7. REAGENTS AND STANDARDS

7.1. Standards

7.1.1. Target Calibration Standards

7.1.1.1. pH 4, 7, and pH 10 buffers, purchased

7.1.1.2. Fresh buffers are poured and used each working day.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. Samples should be analyzed as soon as possible after sampling, but not to exceed twenty-four hours.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS and Sample Duplicate) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Sample Duplicate

9.2.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.2.2. Sample duplicates are performed at a frequency of 10% and must meet laboratory-specific limits for precision.

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each analytical batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A commercially available (Environmental Resource Associates or equivalent) control standard will be analyzed. Recovery must be within +/- 2% of true value.

9.3.3. Corrective Action for LCS

9.3.3.1. If the pH is outside the established control limits the system is out of control and corrective action must occur.

9.3.3.2. Corrective action consists of identification and correction of the cause for the out of control situation and reanalysis of all effected samples.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. Refer to the manufacturer's manual for instrumental calibration.

10.1.2. The following procedure is applicable for use with the Orion 250 pH meter.

10.1.2.1. Rinse the electrodes with reagent water and place in the pH 4.0 buffer. Press "Cal". Allow the value to stabilize and then, using the arrow keys, adjust the value up or down to read 4.00. Press Enter.

10.1.2.2. Rinse the electrodes and place in the pH 7.0 buffer. Allow the value to stabilize and then, using the arrow keys, adjust the value up or down to read 7.00. Press Enter.

10.1.2.3. Calibration Check: Rinse the electrodes and place in the pH 10.0 buffer. Allow value to stabilize. The pH should be between 9.95 and 10.05 or recalibration is necessary.

NOTE: When analyzing drinking water samples, calibrate as described in section 10.1.2, using the pH 7.0 and pH 10.0 buffers for calibration and the pH 4.0 buffer for the calibration check.

10.1.3The pH meter should be calibrated daily. The calibration is recorded on the analytical logsheet.

10.1.4If the pH meter has been turned off, it must be calibrated prior to use.

10.2. Continuing Calibration

10.2.1. A pH 7 buffer is analyzed before analysis and every ten samples to ensure the calibration remains linear.

10.2.2. The pH meter must be recalibrated if the buffer deviates by more than± 2% If this range is exceeded, reanalyze all samples analyzed since the last pH buffer that met criteria.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Waters

11.3.1.1.No preparation necessary for waters and wastewaters.

11.3.2. Solids and Soils

11.3.2.1.Place 20 g (± 0.5 g) of sample in a beaker or other suitable container.

11.3.2.2. Add 20 mL of reagent water and mix for five minutes.

11.3.2.3. Allow sample to stand for one hour to allow the solids to settle out.

11.4. Sample Analysis

11.4.1. Manual Procedure

11.4.1.1. Waters

11.4.1.1.1. Place the sample in a clean beaker using a sufficient volume to cover the sensing elements of the electrode(s). Allow the pH to stabilize (swirling or stirring may quicken stabilization). Record the pH on the analytical logsheet. Remove the electrodes from the sample. Rinse and gently dab off the electrodes between each measurement. Store the electrodes in pH 7 buffer when not in use.

11.4.1.2. Solids

11.4.1.2.1. Immerse the pH electrodes in the supernatant layer of the sample - be careful not to stir up solids. Allow pH to stabilize and record it on the analytical logsheet. Remove and rinse the electrodes between each measurement. Store electrodes in the pH 7.0 buffer.

NOTE: If the sample contains oil or other substances that will coat or damage the electrodes, the pH should be analyzed following SOP# NC-WC-0009, pH - Paper Method.

11.4.2. Automated Procedure

11.4.2.1. Load the appropriate schedule on the autotitrator, starting with the pH calibration.

11.4.2.2. Pour a homogenized sample into the centrifuge tubes and place the tubes in the appropriate position on the autosampler. Remember to include a pH 7 buffer check after every ten positions.

11.4.2.3. Start the autotitrator.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards and any corrective actions or modifications to the method.

11.5.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not Applicable

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Solvent waste must be disposed of in clearly labeled waste cans.

15.2. Acid waste must be collected in clearly labeled acid waste containers.

15.3. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4. Refer to the Laboratory Sample and Waste Disposal plan.

15.5. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, pH Electrometric Measurement, Method 9040B

16.1.2. EPA 600, Methods for Chemical Analysis of Water and Wastes, pH (Electrometric), Method 150.1

16.1.3. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, Soil pH, method 9045C.

16.1.4. STL North Canton Laboratory Quality Manual (LQM), current version

16.1.5. Corporate Quality Management Plan (QMP), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. A minimum reporting limit is not listed in LIMS. Units are reported as No Units.

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Implementation Date 11-22-04

SOP No. NC-WC-0010
Revision No. 6
Revision Date: 10/27/04
Page 1 of 11

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PH ELECTROMETRIC METHOD

(SUPERSEDES: REVISION 5, DATED 02/05/03)

Prepared by: _____ 11/16/04 Date

Reviewed by: _____ 11/16/04 Date
Technology Specialist

Approved by: _____ 11/19/04 Date
Quality Assurance Manager

Approved by: _____ 11-3-04 Date
Environmental Health and Safety Coordinator

Approved by: _____ 11/22/04 Date
Laboratory Director

Proprietary Information Statement:

TABLE OF CONTENTS

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of pH in waters, wastewaters, and solids. It is based on SW846 Methods 9040B and 9045C and EPA Method 150.1. The approximate working range is 1 - 14 pH units. Samples with a pH of < 1 are reported as < 1.

1.2. The associated method codes are PU (9040B), OZ (9045C), and AJ (150.1). The preparation codes are 88 and 1C.

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. The pH is determined electrometrically by using an electrode. The pH meter is calibrated with a series of known pH buffers.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

4. INTERFERENCES

4.1. Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. There are no materials used in this method that have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees

must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents {as well as glassware cleaning procedures that involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of an STL North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. pH meter with electrode(s) and temperature compensation

6.2. Beakers: various

6.3. Top loading balance: Capable of accurately weighing ±0.01 g

6.4. Stir plate and stir bars

6.5. Shaker or mechanical tumbler

6.6. Autotitrator

6.7. Centrifuges tubes

7. REAGENTS AND STANDARDS

7.1. Standards

7.1.1. Target Calibration Standards

7.1.1.1. pH 4, 7, and pH 10 buffers, purchased

7.1.1.2.Fresh buffers are poured and used each working day.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. Samples should be analyzed as soon as possible after sampling, but not to exceed twenty-four hours.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS and Sample Duplicate) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Sample Duplicate

9.2.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the

same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.2.2. Sample duplicates are performed at a frequency of 10% and must meet laboratory-specific limits for precision.

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each analytical batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A commercially available (Environmental Resource Associates or equivalent) control standard will be analyzed. Recovery must be within +/- 2% of true value.

9.3.3. Corrective Action for LCS

9.3.3.1. If the pH is outside the established control limits the system is out of control and corrective action must occur.

9.3.3.2. Corrective action consists of identification and correction of the cause for the out of control situation and reanalysis of all effected samples.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. Refer to the manufacturer's manual for instrumental calibration.

10.1.2. The following procedure is applicable for use with the Orion 250 pH meter.

10.1.2.1. Rinse the electrodes with reagent water and place in the pH 4.0 buffer. Press "Cal". Allow the value to stabilize and then, using the arrow keys, adjust the value up or down to read 4.00. Press Enter.

10.1.2.2. Rinse the electrodes and place in the pH 7.0 buffer. Allow the value to stabilize and then, using the arrow keys, adjust the value up or down to read 7.00. Press Enter.

10.1.2.3. Calibration Check: Rinse the electrodes and place in the pH 10.0 buffer. Allow value to stabilize. The pH should be between 9.95 and 10.05 or recalibration is necessary.

NOTE: When analyzing drinking water samples, calibrate as described in section 10.1.2, using the pH 7.0 and pH 10.0 buffers for calibration and the pH 4.0 buffer for the calibration check.

10.1.3 The pH meter should be calibrated daily. The calibration is recorded on the analytical logsheet.

10.1.4 If the pH meter has been turned off, it must be calibrated prior to use.

10.2. Continuing Calibration

10.2.1. A pH 7 buffer is analyzed before analysis and every ten samples to ensure the calibration remains linear.

10.2.2. The pH meter must be recalibrated if the buffer deviates by more than ± 2% If this range is exceeded, reanalyze all samples analyzed since the last pH buffer that met criteria.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Waters

11.3.1.1. No preparation necessary for waters and wastewaters.

11.3.2. Solids and Soils

11.3.2.1. Place 20 g (± 0.5 g) of sample in a beaker or other suitable container.

11.3.2.2. Add 20 mL of reagent water and mix for five minutes.

11.3.2.3. Allow sample to stand for one hour to allow the solids to settle out.

11.4. Sample Analysis

11.4.1. Manual Procedure

11.4.1.1. Waters

11.4.1.1.1. Place the sample in a clean beaker using a sufficient volume to cover the sensing elements of the electrode(s). Allow the pH to stabilize (swirling or stirring may quicken stabilization). Record the pH on the analytical logsheet. Remove the electrodes from the sample. Rinse and gently dab off the electrodes between each measurement. Store the electrodes in pH 7 buffer when not in use.

11.4.1.2. Solids

11.4.1.2.1. Immerse the pH electrodes in the supernatant layer of the sample - be careful not to stir up solids. Allow pH to stabilize and record it on the analytical logsheet. Remove and rinse the electrodes between each measurement. Store electrodes in the pH 7.0 buffer.

NOTE: If the sample contains oil or other substances that will coat or damage the electrodes, the pH should be analyzed following SOP# NC-WC-0009, pH - Paper Method.

11.4.2. Automated Procedure

11.4.2.1. Load the appropriate schedule on the autotitrator, starting with the pH calibration.

11.4.2.2. Pour a homogenized sample into the centrifuge tubes and place the tubes in the appropriate position on the autosampler. Remember to include a pH 7 buffer check after every ten positions.

11.4.2.3. Start the autotitrator.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards and any corrective actions or modifications to the method.

11.5.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not Applicable

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acidic and alkaline sample waste and exhausted buffer solutions poured down the drain if the pH is between 4 and 10. Any sample waste generated that is not in this pH range is collected in a designated container identified as "Acid Waste".

15.2.1.2. Exhausted soil or oil samples analyzed by the method. The liquid layer is decanted and disposed of in a designated container identified as "Acid Waste". The remaining solid layer is disposed of by placing it in a container identified as "Solid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, pH Electrometric Measurement, Method 9040B

16.1.2. EPA 600, Methods for Chemical Analysis of Water and Wastes, pH (Electrometric), Method 150.1

16.1.3. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, Soil pH, method 9045C.

16.1.4. STL North Canton Laboratory Quality Manual (LQM), current version

16.1.5. Corporate Quality Management Plan (QMP), current version.

16.1.6. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. A minimum reporting limit is not listed in LIMS. Units are reported as No Units.

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Implementation Date: 12/16/04

SOP No. NC-WC-0061
Revision No. 1.3
Revision Date: 12/01/04
Page 1 of 16

STL NORTH CANTON

STANDARD OPERATING PROCEDURE

TITLE: REACTIVE SULFIDE

(SUPERSEDES: (REVISION 1.2, DATED 04/19/02)

Prepared by: _____ 12/13/04 Date

Reviewed by: _____ 12/13/04 Date
Technology Specialist

Approved by: _____ 12/15/04 Date
Quality Assurance Manager

Approved by: _____ 12-8-04 Date
Environmental Health and Safety Coordinator

Approved by: _____ 12/14/04 Date
Laboratory Director

Proprietary Information Statement:

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TABLE OF CONTENTS

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Reactive Sulfide in all wastes, with the condition that wastes combined with acids do not form explosive mixtures. It is based on SW846 Section 7.3.4.2. The lower detection limit is 500 mg/kg. The EPA guidance level is 500 mg H_2S/Kg waste (Total releasable sulfide).

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

1.3. The QuantIMs associated method code is GJ. The preparation code for samples is 08.

2. SUMMARY OF METHOD

2.1. An aliquot of sample is acidified in a closed system. The gas is generated and trapped in a sodium hydroxide solution and then analyzed using the titration method for Sulfide.

2.2. This procedure releases only the hydrogen sulfide evolved under the test conditions. It is not intended to measure forms of sulfide other than those that are evolvable under the test conditions.

3. DEFINITIONS

3.1. Refer to the glossary in the STL Laboratory Quality Manual (LQM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Oxidizers and reducers interfere with Sulfide analysis.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. **Sodium Sulfide will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal.**

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydra-dator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.

Sodium Sulfide	Corrosive	10 ppm-TWA 15 ppm-STEL	Will **form** **H**ydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. All samples with pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Reactivity round bottom flask: 3-neck, 500 mL min. capacity

6.2. Addition funnel: 250 mL pressure-equalizing

6.3. Stir plate and stir bars

6.4. Compressed nitrogen and Two-way regulator with flexible tubing

6.5. Scrubber and absorber tube: 50 mL capacity

6.6. Burettes: 10 mL and 25 mL Class A

6.7. Erlenmeyer Flasks: various

6.8. Pipettes: various

6.9. Graduated cylinders: various

6.10. Analytical balance, capable of accurately weighing ± 0.001g

6.11. 250 mL volumetric flasks

7. REAGENTS AND STANDARDS

7.1.1. Sulfuric Acid, 0.05 M H_2SO_4: Add 2.8 mL concentrated sulfuric acid to a 1 liter volumetric flask containing 900 mL reagent water and bring to volume with reagent water.

7.1.2. Sulfuric Acid, 0.005 M H_2SO_4 (0.01N): Add 100 mL 0.05 M H_2SO_4 to a 1 liter volumetric flask and bring to volume with reagent water.

7.1.3. Sodium Hydroxide, 1.25 N NaOH: Add 50 g sodium hydroxide to a 1 liter volumetric flask and bring to volume with reagent water.

7.1.4. Sodium Hydroxide, 0.25 N NaOH: Add 200 mL 1.25 N NaOH to a 1 liter volumetric flask and bring to volume with reagent water.

7.1.5. Iodine Solution, 0.028 N: Manufactured., or 0.025 N prepared. Add 20 g KI (potassium iodide) and 3.2 g iodine to a 1 liter volumetric flask. Add 500 - 700 mL of reagent water and dissolve. Dilute to volume with reagent water. Store in a dark container. A commercially prepared solution may also be used.

7.1.5.1. Standardization Iodine Solution: Prepare three (3) method blanks using 250 mL of reagent water. Follow the analysis procedure and calculate an average normality.

$$\text{Normality Iodine} = \frac{(\text{Normality } Na_2S_2O_3)(\text{mL of titrant } Na_2S_2O_3)}{20 \text{ mL Iodine}}$$

7.1.6. Sodium Thiosulfate, 0.025 N: Manufactured, or add 0.4 g of NaOH and 6.205 g of sodium thiosulfate ($Na_2S_2O_3 \bullet 5H_2O$) to 500 mL of reagent water in a 1 liter volumetric flask. Dilute to volume with reagent water. Store in a dark container. A commercially prepared solution may also be used.

7.1.6.1. Standardization of 0.025 N Sodium Thiosulfate Solution: To make 0.025N Biiodate Solution, dissolve 0.4062 g $KH(IO_3)_2$ in 500 mL reagent water. Weigh 2 g KI in a 500 mL Erlenmeyer flask. Add 100 to 150 mL reagent water, 5 drops H_2SO_4, and 20 mL biodate solution using a volumetric pipet. Dilute to 200 mL with reagent water. Titrate with Sodium Thiosulfate. When a pale straw yellow color is reached, add 1-2

mL starch. Continue titrating from a blue to a clear end point. Repeat two (2) more times. Calculate an average normality.

$$Na_2S_2O_3 \text{ Normality} = \frac{(a)(b)}{c}$$

where:

a = mLs Biodate (20mL)

b = Normality Biodate (0.025N)

c = mLs of $Na_2S_2O_3$ used to titrate

7.1.7. Starch Indicator: Add 10 mL reagent water to 5 g potato starch and mix. Add mixture to 500 mL boiling reagent water, mix, and cool. Alternatively, a commercially prepared solution may be used.

7.1.8. Hydrochloric Acid, 6 N: Add 250 mL concentrated hydrochloric acid to 250 mL reagent water.

7.1.9. Zinc Acetate Solution: Add 220 g Zinc Acetate to a 1000 mL volumetric flask and dilute to volume with reagent water. Alternatively, a commercially prepared solution may be used.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are unpreserved.

8.2. Samples are stored in glass containers at 4°C ± 2°C.

8.3. There is no defined holding time.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (Method Blank, Sample Duplicate) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All

samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A blank consisting of 10 g of Kaolin must be reacted and analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.1.1. The LCS solution is prepared by adding 3.5 g Na_2S to a 250mL volumetric flask and bringing to volume with 0.01N NaOH. 1.25mL of this solution is added to the LCS sample.

9.3.2. Corrective Action for LCS

9.3.2.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.2.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.2.3. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.1.1. The MS/MSD solution is prepared by adding 3.5 g Na_2S to a 250mL volumetric flask and bringing to volume with 0.01N NaOH. 1.25mL of this solution is added to the MS/MSD samples.

9.4.2. Corrective action for MS/MSDs

9.4.2.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.2.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page 'NC The recovery and/or RPD

were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."

9.4.2.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the laboratory limits.

9.4.2.4. If client program requirements specify to confirm matrix interference's, reprepparation and reanalysis of the MS/MSD may be necessary.

9.5. QC Acceptance Criteria

9.5.1. Control limits are established by the laboratory as described in NC-QA-0018.

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documents as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Summary

11.3.1.1. The sample is acidified in a closed system and liberated Sulfide gas is trapped in 0.25 N NaOH.

11.3.2. Sample Preparation Procedure

11.3.2.1. Add 50 mL 0.25 N NaOH to the absorber tube and connect the scrubber.

11.3.2.2. Add 10 g ± 0.05 g of sample to the reactivity flask.

11.3.2.3. Add 250 mL of 0.005 M H_2SO_4 to the addition funnel.

11.3.2.4. Add spike solutions to LCS, MS, and MSD samples.

11.3.2.5. Close the entire system and begin the flow of nitrogen. The flow should be 3-5 bubbles per second.

11.3.2.6. Begin sample stirring and start the addition of acid to the flask.

NOTE: The stirring should not be fast enough to create a vortex and should be at a constant speed.

11.3.2.7. Begin timing for thirty minutes. Document mixing time.

11.3.2.8. After the thirty minute reacting period, disconnect the system and shut off the nitrogen.

11.3.2.9. Pour the scrubber contents into a 250 mL volumetric flask. Rinse the scrubber with 0.25N NaOH and pour the rinsate into the 250 mL volumetric flask. Bring to volume with 0.25N NaOH.

11.4. Sample Analysis

11.4.1. Pour 100 mL of scrubber into a 500 mL Erlenmeyer flask and add 150 mL of reagent water. Add 1-2 mL of zinc acetate solution, 20.0 mL of 0.025 N iodine (for the addition of the iodide solution, make sure the tip of the pipette is below the surface of the sample), 2-3 mL of 1:1 HCl, and 2 - 3 mL of starch indicator to solution and mix. Titrate with 0.025 N sodium thiosulfate until blue color disappears. Record the volume of titrant used.

11.4.2. Preliminary Evaluation

11.4.2.1. The color of the scrubber solution should be a golden color after the addition of the iodine and HCl; if it is not, additional Iodine solution is needed to keep the color consistent. The additional amount of Iodine then needs to be taken into account in the calculation.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMS after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ***mg / L Sulfide in scrubber solution*** $= \dfrac{[(A \bullet a) - (B \bullet b)]16{,}000}{C} = X$

Where:

A = mL of iodine used

a = N of iodine

B = mL titrant used

b = N of titrant

C = mL of scrubber solution titrated

12.2. ***Reactive Sulfide (mg/kg)*** $= \dfrac{(X)(L)}{(W)}$

Where:

X = Concentrated Sulfide from 12.1

L = Total volume of scrubber solution in liters (0.05 L)

W = Weight of original sample used in kg (0.01 kg)

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.3. The following waste streams are produced when this method is carried out.

15.3.1. Acidic sample waste generated by sample digestion. This waste is collected in the laboratory in a designated container identified as "Acid Waste".

15.3.2. Alkaline sample waste remaining in scrubbers. This waste is collected in the laboratory in a designated container identified as "Alkaline Waste".

15.3.3. Alkaline H_2S waste generated by sulfide titration. This waste is collected in the laboratory in a designated container identified as "Alkaline Waste".

15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test methods for Evaluating Solid Wastes, 3rd Edition, Reactivity, Method 7.3.4.2 for Sulfide.

16.1.2. SW846, Test Methods for Evaluating Solid Wastes, 3rd Edition,

16.1.3. Reactivity, Method 9030B for Sulfide Distillation, Method 9034 for Sulfide Titration.

16.1.4. STL North Canton Laboratory Quality Manual (LQM), current version.

16.1.5. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs

16.2.1. Sulfide, NC-WC-0060

16.2.2. Reactive Cyanide, NC-WC-0033

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

16.3. Withdrawal of Reactive Cyanide and Sulfide, USEPA Office of Solid Waste and Emergency Response Abstract, April 21, 1998.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) is 500 mg/kg Reactive Sulfide.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method Deviation

17.2.1. A rotometer for monitoring nitrogen gas flow rate is not utilized by the laboratory.

17.2.2. A sulfide reference solution is not utilized by the laboratory.

17.2.3. Note that bottles may be received with headspace. In addition, multiple tests may be analyzed from the same container resulting in headspace at the time of analysis.

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Implementation Date: 11-17-04

SOP No. NC-WC-0033
Revision No. 2.2
Revision Date: 11/09/04
Page 1 of 15

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: REACTIVE CYANIDE

(SUPERSEDES: REVISION 2.1, DATED 04/19/02)

Prepared by: _____ 11/16/04
Date

Approved by: _____ 11/16/04
Technology Specialist Date

Approved by: _____ 11/16/04
Quality Assurance Manager Date

Approved by: _____ 11-15-04
Environmental Health and Safety Coordinator Date

Approved by: _____ 11/16/04
Laboratory Director Date

Proprietary Information Statement:

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TABLE OF CONTENTS

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Reactive Cyanide in all wastes, with the condition that wastes combined with acids do not form explosive mixtures. It is based on SW846 Section 7.3.3.2 The working linear range is 10 to 1000 mg/kg. The EPA guidance level is 250 mg HCN/Kg waste (Total releasable cyanide).

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary. The applicable LIMs method code is GI. The preparation code for samples is 08.

2. SUMMARY OF METHOD

2.1. An aliquot of sample is acidified in a closed system. The gas generated is trapped in a sodium hydroxide solution and then analyzed using the titration method for Cyanide.

2.2. This test measures only the hydrocyanic acid evolved under the test conditions. It is not intended to measure forms of cyanide other than those that are evolvable under the test conditions.

3. DEFINITIONS

3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM), current version.

4. INTERFERENCES

4.1. Method interfererences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Sulfide interferes with analysis and can be precipitated out using cadmium carbonate prior to titration.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety manual and this document.

5.2. Potassium Cyanide will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.

5.3. Sodium Sulfide will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Potassium Cyanide	Poison Corrosive	5 Mg/M3 TWA as CN	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.

Sulfuric Acid	Corrosive Oxidizer Dehydra-dator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Sulfide	Corrosive	10 ppm-TWA 15 ppm-STEL	Will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.6. Exposure to chemicals must be maintained **as low as reasonably achievable,** therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.7. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Round Bottom Reactivity flask: 3-neck, 500 mL minimum capacity

6.2. Addition funnel: 250 mL pressure-equalizing

6.3. Stir plate and stir bars

6.4. Compressed Nitrogen and two-way regulator, with flexible tubing.

6.5. Scrubber and absorber tube: 50 mL capacity

6.6. Buret: 10 mL Class A

6.7. Erlenmeyer flasks: various

6.8. Volumetric flasks: various

6.9. Graduated cylinders: various

6.10. Whatman filter paper #4

6.11. Analytical balance, capable of accurately weighing ±0.001g.

6.12. Lead Acetate test strips.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sulfuric Acid: (H_2SO_4), concentrated, reagent grade

7.1.2. 0.05 M H_2SO_4: Add 2.8 mL concentrated H_2SO_4 to 900 mL reagent water and dilute to 1 liter with reagent water.

7.1.3. 0.005 M H_2SO_4 (0.01N): Add 100 mL 0.05 M H_2SO_4 to 800 mL reagent water and dilute to 1 liter with reagent water.

7.1.4. Sodium Hydroxide: (NaOH), reagent grade

7.1.5. 1.25 N NaOH: Add 50 g NaOH to 900 mL reagent water and dilute to 1 liter with reagent water.

7.1.6. 0.25 N NaOH: Add 200 mL 1.25 N NaOH to 700 mL reagent water and dilute 1 liter with reagent water. A commercially prepared solution may also be used.

7.1.7. 0.0192 N Silver Nitrate Solution: reagent grade

7.1.8. Rhodanine Indicator: Dimethylaminobenzalrhodanine, reagent grade

7.1.9. Kaolin: reagent grade

7.1.10. Cadmium Carbonate: ($CdCO_3$), reagent grade

7.1.11. Spiking Solution (LCS, MS/MSD): Add 1.25g KCN to a 250mL volumetric flask. Bring to volume with 0.01N NaOH.

7.1.12. 0.01N NaOH: Add 0.4g NaOH to a 1 L volumetric flask. Bring to volume with reagent water.

8. SAMPLE PRESERVATION AND STORAGE

8.1. Samples are stored in plastic or glass containers at 4° ± 2°C.

8.2. Solid and water samples are not chemically preserved.

8.3. There is no defined holding time.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, MS, MSD, Method Blanks) which are processed similarly, with respect to the procedure. All samples within the batch must be treated with the same lots of reagents and the same processes. All samples within the batch must be treated with the same lot of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A blank consisting of 10 g Kaolin or other inert solid must be reacted and analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to

monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. Corrective Action for LCS

9.3.2.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.2.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.2.3. Corrective action will be reprepparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. Corrective action for MS/MSDs

9.4.2.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include reprepparation and reanalysis of the batch.

9.4.2.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page 'NC The recovery and/or RPD were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."

9.4.2.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the laboratory limits.

9.4.2.4. If client program requirements specify to confirm matrix interference's, repreparation and reanalysis of the MS/MSD may be necessary.

9.5. QC Acceptance Criteria

9.5.1. Control limits are established by the laboratory as described in NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOPs S-Q-003 and NC-QA-0021.

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Summary

11.3.1. The sample is acidified in a closed system and liberated Cyanide gas is trapped in 0.25 N NaOH.

11.4. Sample Preparation Procedure

11.4.1. Add 50 mL 0.25 N NaOH to the absorber tube and connect the scrubber.

11.4.2. Add 10 g ± 0.05 g approximately of sample (waters and non-waters) to the reactivity flask with closed stop cock.

11.4.3. Add 250 mL of 0.005 M H_2SO_4 to the addition funnel.

11.4.4. Add 1.25 mL of spiking solution to LCS, MS, and MSD samples.

11.4.5. Close the entire system and begin the flow of nitrogen. The flow should be 3-5 bubbles per second.

11.4.6. Begin sample stirring and start adding the acid by opening the stopcock on the separatory funnel. **NOTE:** The stirring should not be fast enough to create a vortex and should be at a constant speed.

11.4.7. Allow the sample to react (while mixing) for thirty minutes. Document mixing time.

11.4.8. After the thirty minute reacting period, disconnect the system and shut off the nitrogen.

11.4.9. Pour the scrubber contents into a 250 mL volumetric flask. Rinse the scrubber with 0.25N NaOH and pour the rinsate into the 250 mL volumetric flask. Dilute to volume with 0.25N NaOH.

11.5. Preparation Documentation

11.5.1. Record all the necessary information on the analytical logsheet.

11.6. Sample Analysis Procedure

11.6.1. After the 100 mL aliquot has been removed, check the scrubber solution with lead acetate test paper for the presence of sulfide. If negative for sulfide, go to Section 11.4.2. If positive for sulfide,add one scoop (1 - 2 g) of $CdCO_3$ powder to the volumetric flask and mix. If the precipitate turns yellow, add another scoop until white precipitate forms. This removes sulfide which interferes with the titration. All QC and field samples must be treated for sulfide prior to cyanide analysis.

11.6.2. Add 10-12 drops of rhodanine indicator to the Erlenmeyer flask. The solution should turn yellow. Titrate with 0.0192 N silver nitrate until a orange-peach color develops. Record the volume of titrant used on the analytical logsheet. Filter 100 mLs of treated scrubber solution through a #4 Whatman filter paper into an Erlenmeyer flask.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

$$HCN(mg/kg) = (X * L) \div W$$

Where:

X= concentration CN (mg/L) = {[mL titrant (sample) – mL titrant (blank)]/mL sample titrated}X 100

L = volume of solution in scrubber

W = weight of sample used

12.2. Report Documentation

12.2.1. Record all analytical information on the analytical logsheet, including the analytical data from standards, blanks, and LCSs.

12.2.2. All standards are logged onto the departmental standard logsheet. All standards are assigned in an unique number for identification. Logbooks are reviewed by the supervisor or designee.

12.2.3. The documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, ect.) and daily calibration data corresponding to all final runs is available for each data file.

12.2.4. Sample results and associated QC are entered into the LIMS after final technical review.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. **Aqueous waste generated by the analysis.** Aqueous waste can be poured down the drain if the pH is between 4 and 10. Any sample waste generated that is not in this pH range must be collected and disposed of in the designated acid waste drum located in the lab. This waste is collected in the laboratory in a designated container identified as "Acid Waste".

15.2.1.2. Samples that are above the reporting limit are disposed of in designated waste container labeled "Cyanide Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

16. REFERENCES

16.1. References.

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Reactivity, Method 7.3.3.2 for Cyanide Reactivity, and its Updates.

16.1.2. SW846, Test Methods for Evaluating Solid Wastes, Reactivity, Method 9012A for Cyanide Analysis, and its Updates.

16.1.3. STL North Canton Laboratory Quality Manual (LQM), current version.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. STL Laboratory Quality Manual (LQM), current version.

16.1.6. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs

16.2.1. Cyanide, Total NC-WC-0031

16.2.2. Reactive Sulfide, NC-WC-0061

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

16.2.4. QA Policy, QA-003

16.2.5. Glassware Washing, NC-QA-0014

16.2.6. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.7. Navy/Army SOP, NC-QA-0016

16.3. Withdrawal of Reactive Cyanide and Sulfide, USEPA Office of Solid Waste and Emergency Response Abstract, April 21, 1998.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Troubleshooting Guide

17.1.1. If the sample turns black while titrating, sulfide is present. See Sample Analysis Procedure 11.4.1 for removal. Use the remaining aliquot.

17.2. Method Deviation

17.2.1. A rotometer for monitoring nitrogen gas flow rate is not utilized by the laboratory.

17.2.2. A cyanide reference solution is not utilized by the laboratory.

17.2.3. Note that bottles may be received with headspace or multiple tests may be analyzed from the same container resulting in headspace at the time of analysis.

ENVIRONMENTAL TESTING & CONSULTING, INC. – STANDARD OPERATING PROCEDURES

Volatile Organic Compounds by GC/MS

According to SW-846 Method 8260B

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application for Method

1.1 This SOP addresses the determination of certain volatile organics compounds (VOCs) using gas chromatography/mass spectrometry (GC/MS) and assumes that the analyst is familiar with SW 846 Method 8260B.

1.1.1 Applicable Matrices – Wastewater. Method 8620B can be used to determine VOC compounds in a variety of municipal and industrial waters. However, LMP, Inc. defaults to EPA Method 624 for these types of samples.

1.1.2 Applicable Matrices – Groundwater/Soil/Solid Waste/RCRA Waters. Method 8260B can be used to determine VOC compounds in a variety of water and solid waste matrices.

1.2 Analytes that are currently reported using this method are listed in Appendix A #4.

1.3 Detection limits (MDLs – Method Detection Limits; MQLs – Method Quantitation Limits) and control limits for the analytes currently reported using this method are listed in the Analyte Summary Table. Refer to LMP's Determination of MDL/MQL/RL SOP. Detection limits presented are those that can be achieved in the absence of interference.

2.0 Summary of Method

2.1 Method 8260B provides GC and MS conditions for the detection of ppb levels of VOCs. VOCs are introduced to the GC/MS using the following methods

2.1.1 SW 846 Method 5030B. This method is applicable to water samples only.

2.1.2 SW 846 Method 5035. This method is applicable to low level and medium level soils only.

Note: LMP, Inc. defaults to Method 5035 for soil samples.

Method 5030A for soils has been deleted from the current edition of SW-846 and is considered an obsolete method. While many states/agencies/projects do not want or require method 5035, documentation must be maintained that indicates that the client has been notified that method 5035 is the only approved method for soils. Refer to Appendix A #1. All soils received by LMP, Inc. will be preserved and analyzed according to method 5035 specifications.

2.2 GC/MS conditions are presented in Table 7 of this SOP

3.0 Interferences and Potential Problems

3.1 Refer to *Section 3.0 of SW 846 Method 8260B* for further details.

3.2 Method interferences are reduced by proper glassware cleaning procedures Cleaning procedures are detailed in LMP's Organic Laboratory Glassware Cleaning Procedures SOP

3.3 Methylene Chloride - This solvent is used in 95% of all extractions performed by LMP, Inc. Precautions must be taken to minimize ambient laboratory levels in the volatile laboratory

3.3.1 All samples to be analyzed for volatiles (soil or water) must be stored in the refrigerators located in the volatile lab. Samples may not be removed from this lab until all volatile analyses have been completed. For soil samples, a second sub-sample may be provided to perform percent solid determination.

3.3.2 Personnel from the organic extraction lab, and other areas of the laboratory, are not allowed into the volatile lab if they have been in the extraction lab within the previous 8 hours.

3.3.3 Negative pressure must be maintained in the extraction and concentration labs (e.g., ventilation hoods must be in operation at all times.)

3.3.4 Refer to the Quality Manual for procedures on evaluation of method blanks.

3.4 Analyses of reagent blanks provide information about the presence of contaminants. Subtracting blank values from sample results is not permitted.

3.5 Carrier/Purge Gas - Zero Grade Helium. In order to minimize problems associated with contaminated high pressure tanks, the following precautions are taken:

3.5.1 Each system must have a dedicated high-pressure tank and regulator. This isolates each system and minimizes the chance of a single tank affecting more than one (1) instrument.

3.5.2 LMP, Inc. has negotiated with our gas supplier, NexAir, to provide ultra clean, aluminum tanks. These tanks are individually labeled and are only used by LMP, Inc In addition, a check valve is

installed in each tank that will not allow use below 300 PSI.

3.5.3 The analytical baseline is to be monitored daily for the presence of hydrocarbons which may indicate potential gas contamination. The high-pressure tank is to be replaced and returned to the supplier at the first sign of contamination.

4.0 Equipment, Instrumentation and Apparatus

4.1 Refer to *Section 4 of SW 846 Method 8260B.*

4.2 Analytical balance capable of weighing 0.0001g

4.3 Glassware – Micro Syringes, Auto Pipettes and Volumetric Pipettes (Vendor/Cat #) – Items specific to this method are listed in Table 1

4.4 The current configuration of analytical systems for this method is found in Table 7.

5.0 Reagents and Standards

5.1 Reagent grade chemicals are to be used for this method. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Program (SVQAP).

5.3 Reagents – Table 2

5.3.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter 1 of SW-846.

5.4 Stock Certified Solutions – Table 3 - Whenever possible, standard solutions are purchased as certified solutions from an outside source. Each solution is accompanied by certification data on the concentration and traceability of the solution All solutions used in the method are certified solutions.

5.5 Calibration Standards (e.g., WS-1, WS-2) – The initial calibration is performed using ten (10) calibration standards (targets and surrogates). One standard corresponds to the MQL. The remaining standards encompass the working range of the GC/MS system. All quantitatively reported analytes must be included in the calibration standards. Table 3 details the certified solutions currently used. Table 6 details the preparation of the working standards from the certified solutions.

5.6 Surrogate Standards - These solutions are added to all samples prior to analysis or preparation Table 3 details the certified solutions currently used. Surrogate standard preparation is listed in Table 4. Spiking volumes and concentrations are listed in Table 5 The current surrogates used are Dibromofluoromethane, 1, 2-Dichloroethane-d4, Toluene-d8 and 4-Bromofluorobenzene.

5.7 Internal Standard – Internal standards are added to all calibration standards and samples (internal QC and environmental) Table 3 details the certified solutions currently used. Internal standard preparation is listed in Table 4. Spiking volumes and concentrations are listed in Table 5. The current internal standards used are Pentafluorobenzene, 1, 4-Difluorobenzene, Chlorobenzene-d5, 1, 4-Dichlorobenzene-d4.

5.8 4-Bromofluorobenzene (BFB) Standard – GC/MS tune standard. Table 3 details the certified solutions currently used. BFB standard preparation is listed in Table 41.

5.9 Laboratory Control Solution - This standard contains all target analytes and is added to a clean matrix (i.e. blank spike) to monitor overall method performance. Table 3 details the certified solutions currently used LCS standard preparation is listed in Table 4. Spiking volumes and concentrations are listed in Table 5.

5.10 Matrix Spike Solution - This solution contains all target analytes and is added to aliquots of sample (MS/MSD) to monitor sample matrix effects. Table 3 details the certified solutions currently used. MS standard preparation is listed in Table 4. Spiking volumes and concentrations are listed in Table 5

5.11 Standards and standard solutions are stored at –10°C to –20°C.

5.11.1 The permanent gas standard should be prepared fresh as needed (Table 4) if CV checks indicates a chronic problem

5.11.2 Non-gas standards should be prepared fresh every six months or earlier if the CV analysis indicates a chronic problem.

6.0 Health and Safety

6.1 Each chemical compound/reagent/standard should be treated as a potential health hazard. MSDS forms for the standards/reagents used in this method are available from the Quality Assurance Officer (QAO). Refer to the Chemical Hygiene Plan SOP (CHP) for overall guidance.

6.2 In accordance with the *OSHA Laboratory Standard, 29 CFR 1910.1450*, LMP, Inc., has implemented a written Laboratory Safety Plan that is accessible to all employees. Consult this document for details on health and safety as it applies to the activities described in the SOP.

7.0 Sample Preservation and Containers

7.1 As a rule, LMP, Inc. does not engage in sampling activities and may not have control of field sampling activities conducted by clients. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements, which are essential to ensure the validity of the laboratory's data. Refer to LMP's Sample Login Procedures SOP.

7.2 Sample Collection

7.2.1 *Water samples* are collected in 40 mL amber, Teflon-lined septum vials with no headspace (3 per sample). Vials are preserved with hydrochloric acid. Samples must be stored 4°C±2 from time of sampling until analysis.

7.2 2 *Soil samples* are collected according to method 5035. Refer to LMP's SW 846 Method 5035 SOP. For any option, samples must be stored at 4°C±2 from time of sampling until analysis. The options are summarized below:

- ❑ Option 1. For each soil sample. Three (3), 5-gram EnCore samplers and one (1) 4oz glass container. (The 4oz container is for solids determination and may or may not be provided by the client.) The EnCores must be received and preserved by the laboratory within 48 hours of collection. Two (2) of the EnCores are to be preserved for low-level analysis with sodium bisulfate. One (1) of the EnCores is to be preserved with methanol for possible medium-level analysis.
- ❑ Option 2. For each soil sample: Two (2), pre-weighed 40 mL septum vials containing 5 mL of sodium bisulfate solution and a stir bar; One (1), pre-weighed 40 mL septum vial containing 5 mL of methanol, One (1) 4oz glass container, if applicable.
- ❑ Option 3 This option is no longer officially recognized according to SW-846. However, many states/agencies/projects will continue to use the option of collecting soils in 4oz or 9oz Teflon-lined wide-mouth glass containers. Samples must be stored at 4°C±2 from time of sampling until analysis. Samples arriving at the laboratory using this option will be processed according to Method 5035 preservation and holding time requirements.

7.3 Holding Time

7.3.1 Holding time for this analysis is defined as the number of days from sample collection in the field to date analyzed by the instrument.

7.3.2 Water samples must be analyzed within 14 days of collection.

7.3.3 Soil samples must be analyzed within 14 days of collection

8.0 Calibration and Standardization

8 1 Prior to initial calibration, it is highly recommended that full system maintenance be performed. Performing the initial calibration is an expensive and vital procedure. If the system is not operating properly for the analysis of standards, it will not be possible to generate quality data during the analysis of samples Make sure the analytical system is optimized prior to initial calibration.

8.2 Operating conditions for the GC/MS system are provided in Table 7.

8 3 Injection port maintenance is performed at the discretion of the analyst, prior to beginning the analytical sequence. All maintenance performed is documented in the appropriate system maintenance log. For VOC instrumentation, all items below need not be performed at a specific interval. Unless specified otherwise, it is recommended that these options be performed as needed.

- ❑ Replace injection port liner
- ❑ Replace injection port disc
- ❑ Replace injection port septa.
- ❑ Clip approximately 1 to 2 inches of column/guard column (performed only as needed). This step can potentially cause a shift in retention times. The BFB tune must be monitored for any shift in retention times.
- ❑ Bake GC at 250°C for a minimum of 1 hour. - Daily
- ❑ Injection port maintenance should be performed as early in the morning as possible to allow the GC to bake for as long as possible prior to beginning the analytical sequence.

8.4 GC/MS Instrument Performance Check Bromofluorobenzene (BFB)

8.4.1 Each GC/MS system must be hardware-tuned to meet the BFB tune criteria in Table 8. Each analytical sequence must begin with a system performance test. 50ng of BFB is injected or purged. The mass spectrum of BFB must meet the m/z criteria in Table 8 before any samples, blanks or standards are analyzed. The following options are available when evaluating the BFB peak:

- ❑ Use a single scan to evaluate against BFB criteria.
- ❑ Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak.

8.5 Initial Calibration (ICAL). Working standards for the initial calibration are prepared just prior to calibration. Standards include all target analytes, surrogates and internal standards. Working standards used are listed in Table 6. Peak areas are used for each target/surrogate. The internal standard technique is used for this calibration.

8.6 Aqueous Initial Calibration

A series of 10 calibration standards are analyzed to generate the initial calibration using the internal standard approach.

- ❑ Add organic free water to the 10cc syringe and adjust to 10mL. The initial calibration is based on a 10mL purge volume.
- ❑ Spike the syringe, per Table 6A, with the appropriate amount of target analyte standard solution. Always proceed from the lowest working standard to the highest.
- ❑ Spike the syringe, per Table 6A, with the appropriate amount of surrogate standard solution. Surrogates are calibrated the same as target analytes. A separate surrogate solution is used for the initial calibration process.
- ❑ Internal standard solution is added automatically by the Archon autosampler.
- ❑ Transfer sample to 40mL vial and load onto Archon autosampler.

8.7 Soil Initial Calibration

A series of 10 calibration standards are analyzed to generate the initial calibration using the internal standard approach.

- ❑ Add organic free water to the 10cc syringe and adjust to 5mL. The initial calibration is based on a 5mL purge volume.
- ❑ Spike the syringe, per Table 6B, with the appropriate amount of target analyte standard solution. Always proceed from the lowest working standard to the highest.
- ❑ Spike the syringe, per Table 6B, with the appropriate amount of surrogate standard solution. Surrogates are calibrated the same as target analytes. A separate surrogate solution is used for the initial calibration process.
- ❑ Internal standard solution is added automatically by the Archon autosampler.
- ❑ Transfer sample to 40mL vial with 0.5g sodium bisulfate and load onto Archon autosampler.

8.8 Standard WS-1 demonstrates a lower MQL for several analytes.

8.9 Standards WS-2 thru WS-10 establishes the working range of the detector. Concentrations found in samples that are above WS-10 must be diluted to be within the working range.

8 10 Initial Calibration (ICAL) Evaluation. Standards are processed using the Target data processing system. An initial calibration report is generated and evaluated using the criteria listed in the following sections. Refer to Appendix A # 4. Response Factors (RFs) are calculated for each target analyte/surrogate standard relative to one of the internal standards (ISTD). The ISTD selected should be the one that has a retention time closest to the analyte being measured. The calculation for RF is provided in Section 10.

8.11 The ICAL must be evaluated against acceptance criteria prior to beginning analysis of samples. A Method Sequence Check List provides an overview of the main acceptance criteria for the initial calibration.

8.11.1 System Performance Check Compounds (SPCCs). Review the Target mean RF for each target analyte from the initial calibration curve. Five compounds (the System Performance Check Compounds or SPCCs) are checked for a minimum average response factor These compounds are chloromethane; 1,1-dichloroethane; bromoform, chlorobenzene; and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system.

8.11.2 Example problems include:

- ❑ Chloromethane is the most likely compound to be lost if the purge flow is too fast.
- ❑ Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.
- ❑ Contaminated transfer lines degrade Tetrachloroethane and 1,1-Dichloroethane in purge-and-trap systems and/or active sites in trapping materials.
- ❑ The minimum mean response factors for the volatile SPCCs are as follows:
- ❑ Chloromethane 0.10
- ❑ 1,1-Dichloroethane 0.10
- ❑ Bromoform 0.10
- ❑ Chlorobenzene 0.30
- ❑ 1,1,2,2-Tetrachloroethane 0.30

8.11.3 Calibration Check Compounds (CCC). The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Review the Target SD and RSD of the RFs for each target analyte and surrogate standard from the initial calibration curve. The calculation is provided in Section 10.

- ❑ The RSD should be less than or equal to 15% for each target analyte However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30% The CCCs are
- ❑ 1,1-Dichloroethene, Toluene, Chloroform, Ethylbenzene, 1,2-Dichloropropane and Vinyl chloride.
- ❑ If an RSD of greater than 30% is measured for any CCC, then the calibration is not valid. Corrective action must be taken before re-attempting calibration.

8.12 Linearity of Target Analytes and Surrogate Standards. If the RSD of the target/surrogate is less than 15%, then linearity through the origin can be assumed and the average RF from the ICAL used for quantitative purposes. If the RSD of any analyte is greater than 15% then the calibration options for the initial calibration as detailed in the Quality Manual must be applied.

8.13 Initial Calibration Verification (ICV). The initial calibration curve is verified as accurate prior to the analysis of samples with a standard prepared from an independent source. This ICV involves the analysis of a mid-range working standard containing all of the target analytes. The ICV standard used is listed in Table 3. This standard is analyzed immediately following an initial calibration and must meet CVI criteria to be acceptable. The ICV may also be used as the CV.

8.14 Calibration Verification (Initial) & CVI. The initial calibration must be verified at the beginning of each analytical sequence or once per 12-hour analytical shift This is performed by the analysis of the mid-range calibration standard, WS-6 for aqueous and WS-5 for soils. All CV reports are generated by the Target data system. The following must be analyzed as part of the CV process:

- ❑ BFB Tune. 50 ng of BFB is injected or purged. The mass spectrum of BFB must meet the m/z criteria in Table 8 before any samples, blanks or standards are analyzed. Refer to 8 4 1
- ❑ Calibration Verification – WS-6 for aqueous and WS-5 for soils

8.14.1 CV - System Performance Check Compounds (SPCCs). The CV must meet SPCC criteria as per section 8.10.1. This check must be met before sample analysis begins.

8.14.2 CV - Calibration Check Compounds (CCC). The validity of the ICAL must be checked Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model Refer to Section 10 for calculations.

- If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed valid, as per Section 8.10.3.
- Evaluate percent difference or drift for all other target analytes/surrogates. LMP, Inc. has established a Max %difference/drift of 30%.
- USCOE projects require that all target analytes be within 20%. CV reports are provided to indicate which analytes are outside the 20% criteria.

8.14.3 Internal Standard Retention Time. The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

8.14.4 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

8.14.5 A Method Sequence Check List provides an overview of the main acceptance criteria for the CVs. Refer to Appendix A #3

8.15 NELAP Requirements for CV evaluation

If the continuing instrument calibration verification results obtained are outside established acceptance criteria, corrective actions must be performed. If routine corrective action procedures fail to produce a second consecutive (immediate) calibration verification within acceptance criteria, then either the laboratory has to demonstrate performance after corrective action with two consecutive successful calibration verifications, or a new initial instrument calibration must be performed. If the laboratory has not demonstrated acceptable performance, sample analyses shall not occur until a new initial calibration curve is established and verified. However, sample data associated with unacceptable calibration verification may be reported as qualified data under the following special conditions:

8.15.1 When the acceptance criteria for the continuing calibration verification are exceeded high, i e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.

8.15.2 When the acceptance criteria for the continuing calibration verification are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted

9.0 Analytical Procedure

9.1 Sample Introduction. Water samples are purged and analyzed according to Method 5030B. Solid samples are purged and analyzed according to Method 5035. Refer to Table 9 for QC objectives.

9.2 GC/MS conditions are provided in Table 7.

9.3 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

9.4 The analytical procedure begins with the daily review of the sample tracking reports. These reports provide information concerning Due Dates and Holding Time Dates. In addition, LIMS result sheets are provided that indicate the method and specific target analytes required. Samples are always prioritized to ensure that holding times are not violated.

9.5 Begin process of completing VOC system Daily Run Log. All analyses for a system are recorded on this log. Refer to Appendix A #2.

9.6 In general, all VOCs are screened using a GC FID/PID screening methods that will provided information about dilutions

9.7 Assemble samples for analysis. Allow samples to come to ambient temperature before proceeding.

9.7.1 Water samples will generally arrive in three (3) septum vials. One vial will be sufficient for sample (MS/MSD if required) analysis. The additional vials should remain in cold storage for future needs (e.g dilution, re-analysis)

9.7.2 Soil samples, by this time, should have been preserved according to Method 5035. Each soil should have two (2) low level vials with a stir-bar, preserved with sodium bisulfate available. A medium level vial preserved with methanol should also be available.

9.8 Water Sequence - Transfer sample from field septum vial to 10cc syringe.

9.8.1 Detection limits and ICAL are based on a 10 mL purge volume.

9.8 2 Check pH and record in Daily Run Log

9.8.3 Sample dilutions can be performed at this stage if needed.

9.8.4 The CV is used as the LCS for this method.

9 8.5 A method blank is prepared and analyzed after the CV/LCS

9.8.6 A MS/MSD is required for each sequence. If sample is a MS/MSD, separate aliquots are poured into separate syringes. The MS/MSD is spiked with the appropriate solution based on Table 5.

9.8 7 Transfer the sample from the syringe to a new, clear, labeled 40 mL septum vial.

9.8.8 Internal Standards/Surrogate Standards. These solutions are added to the sample by the Archon autosampler.

9 9 Soil Sequence

9.9.1 Soils are in pre-weighed and preserved vials. Vials will contain approximately 5 grams of sample. The vial is to be weighed and the actual weight of the sample calculated. Weights are recorded in the Soil Extraction Logbook. Use one (1) of the low level vials for initial analysis. In this case, use the methanol- preserved vial and perform the necessary dilution.

9.9.2 A method blank is prepared and analyzed after the CV/LCS

9.9.3 A separate LCS (and LCSD when enough sample is not available for MS/MSD) is required for each sequence.

9.9.4 A MS/MSD is required for each sequence if enough sample has been provided. The MS/MSD is spiked with the appropriate solution based on Table 5.

9 9 5 Internal Standards/Surrogate Standards. These solutions are added to the sample by the Archon autosampler.

9.10 Complete the Daily Run Log for each sample prepared.

9.11 Load samples onto the Archon autosampler.

9.12 Use of the HP EnviroQuant Data Acquisition software. Refer to Data Processing of Organic Samples SOP.

9.13 Target Data Processing. . Refer to Data Processing of Organic Samples SOP. This SOP details the procedures for identification and quantitation of analytes using the Target data processing system.

9.13.1 Result evaluation. A Method 8260B Sequence Checklist is completed for each analytical sequence Refer to Appendix A #3.

9.14 Results. All results for this method are calculated using the internal standard method calculation provided in Section 10.

9.14 1 Above the highest point in the ICAL, the sample should be diluted and re-analyzed

- ❑ Optimally, the dilution should be performed to bring the concentration of the analyte within the upper range of the ICAL.
- ❑ If a dilution cannot be performed, the result is reported with an "E" flag to indicate that the result exceeds the ICAL range, and a case narrative should accompany the analytical results.

9.14.2 Surrogates. Surrogates are added to each sample, blank, and QC sample and are also contained in each calibration standard.

- ❑ Surrogate retention times are useful in tracking retention time shifts.
- ❑ Recoveries for all surrogates are calculated for method blanks, laboratory control samples, matrix spikes and samples using the recovery calculation listed in Section 10

- ❑ Recoveries for all surrogates should be within acceptance criteria.
- ❑ Corrective action for recovery outliers is detailed in Section 13.

9.14.3 Batch Quality Control (QC) Samples. Each analytical batch will contain QC samples used to evaluate the precision and accuracy of this method. These QC samples are analyzed as part of the sequence and evaluated according to the criteria discussed in Section 11.

9.15 Qualitative Analysis. The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

9.15.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other or the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time.

9.15.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

9.15.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

9.16 Tentatively Identified Compounds (TIC). For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. TICs are provided by default for Level III and IV data packages. TICs are provided for Level I and II data packages only upon request, or to support issues of matrix interference or required initial dilutions. Use the following guidelines for reporting TICs:

9.16.1 Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

9.16.2 The relative intensities of the major ions should agree within ± 20% (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%)

9.16.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

9.16.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

9.16.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks.

9.17 Quantitative Analysis. Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

9.17.1 If the RSD of a compound's response factors is 15% or less, then the concentration in the sample may be determined using the average response factor (RF) from initial calibration curve. Refer to Section 10.

9.17.2 If the RSD of a compound's response factors is > 15%, then the concentration in the sample is determined using linear regression. Refer to Section 10.

9.18 When applicable, the concentration of any non-target analytes identified (TICs) should be estimated. The same formulae should be used with the following modifications: The areas A and A should be from the total ion chromatograms, and x is the RF for the compound should be assumed to be 1. The resulting concentration should be reported indicating:

- ❑ that the value is an estimate, and
- ❑ which internal standard was used to determine concentration.

Use the nearest internal standard free of interferences.

10.0 Calculations

10.1 Initial Calibration – Response Factor (RF)

The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate.
C_{is} = Concentration of the internal standard.

10.2 Initial Calibration – Average Response Factor To evaluate the linearity of the initial calibration, review the mean RF, the standard deviation (SD), and the RSD as follows:

$$\text{mean RF} \quad \overline{RF} \quad \frac{\sum_{i=1}^{n} RF_i}{n} \qquad SD \quad \sqrt{\frac{\sum_{i=1}^{n} (RF - \overline{RF})^2}{n-1}}$$

$$RSD \quad \frac{SD}{\overline{RF}} \times 100$$

RF_i = RF for each of the calibration standards
$\overline{RF}$ = mean RF for each compound from the initial calibration
n = number of calibration standards

10.3 Initial Calibration – Linear Calibration using Least Squares Regression.
The regression will produce the slope and intercept terms for a linear equation (internal standard quantitation) in the form

$$\frac{A_s C_{is}}{A_{is}} = aC_s + b$$

where:

A_s = Area (or height) of the peak for the target analyte in the sample (s)
A_{is} = Area (or height) of the peak for the internal standard (is)
C_s = Concentration of the target analyte in the calibration standard (s)
C_{is} = Concentration of the internal standard (is)
a = Slope of the line (also called the coefficient of C_s)
b = The intercept

In calculating sample concentrations by the internal standard method, the regression equation is rearranged to solve for the concentration of the target analyte (Cs), as shown below:

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a}$$

10.4 Calibration Verification

Calibration verification for linear calibrations involves the calculation of the percent difference of the instrument response between the initial calibration and each subsequent analysis of the calibration verification standard

$$\% \text{ Difference} = \frac{CF_v - \overline{CF}}{\overline{CF}} \times 100 \quad \text{or} \quad = \frac{RF_v - \overline{RF}}{\overline{RF}} \times 100$$

where CF_v and RF_v are the calibration factor and the response factor (whichever applies) from the analysis of the verification standard, and CF and RF are the mean calibration factor and mean response factor from the initial calibration.

10.5 Concentration of Analytes – Aqueous Sample

$$\text{Concentration } (\mu g/L) \quad \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

A_x = Area (or height) of the peak for the analyte in the sample.
V_t = Total volume of the concentrated extract (µL). For purge and trap analysis, V_t is not applicable and therefore is set at 1.
D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is dimensionless.
CF = Mean calibration factor from the initial calibration (area per ng).
V_i = Volume of the extract infected (µL). The nominal injection volume for samples and calibration standards must be the same. For purge and trap analysis, V_i is not applicable and therefore is set at 1. If concentration units are used in calculating the calibration factor, then V_i is not used in this equation.
V_s = Volume of the aqueous sample extracted or purged in mL. If units of liters are used for this term, then multiply the results by 1000.

10.6 Concentration of Samples – Non-aqueous Samples

$$\text{Concentration } (\mu g/kg) \quad \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_i)(W_s)}$$

where A_x, V_t, D, $\overline{CF}$, and V are as described in 7.10.1.1, and

W_s = Weight of sample extracted or purged (g). Either the wet weight or dry weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

10.7 Calculation of Recovery. Accuracy is estimated from the recovery of spiked analytes from the matrix of interest. Laboratory performance in a clean matrix is estimated from the recovery of analytes in the LCS. Calculate the recovery of each spiked analyte in the matrix spike, matrix spike duplicate (if performed) and LCS according to the following formula:

$$\text{Recovery} \cdot \%R \quad \frac{C_s - C_u}{C_n} \times 100$$

Where

C_s = Measured concentration of the spiked sample aliquot
C_u = Measured concentration of the unspiked sample aliquot (use 0 for the LCS)
C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spiked aliquot (for LCS)

10.8 Calculation of Precision Precision is estimated from the relative percent difference (RPD) of the concentrations (not the recoveries) measured for matrix spike/matrix spike duplicate pairs, or for duplicate analyses of unspiked samples. Calculate the RPD according to the formula below.

$$\text{RPD} \quad \frac{| C_1 \quad C_2}{\left(\frac{C_1 \cdot C_2}{2}\right)} \times 100$$

where·

C_1 = Measured concentration of the first sample aliquot.
C_2 = Measured concentration of the second sample aliquot.

10.9 Calculation of Surrogate Recovery:

$$\text{Recovery (\%)} \quad \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) added}} \times 100$$

11.0 Quality Control

11.1 Overall method performance is monitored by the use of various internal quality control checks. These checks are performed at various stages throughout the preparation and analytical process.

11.2 Analysis. The analysis batch is defined as samples of the same or similar matrix that are analyzed together on one instrument within the same 12-hour analytical shift. For VOCs, the preparation and analytical batch are the same. The following internal batch QC samples are included for each batch of samples analyzed using Methods 5030B or 5035:

- ❑ Method Blank (MB) – Evaluate Result
- ❑ Laboratory Control Sample (LCS) – Evaluate Recovery
- ❑ Laboratory Control Sample Duplicate (LCSD) – Evaluate Recovery/RPD. (Performed when insufficient volume of sample is available for MS/MSD.)
- ❑ Matrix Spike (MS) – Evaluate Recovery
- ❑ Matrix Spike Duplicate (MSD) – Evaluate Recovery/RPD

11 3 Analytical Sequence. For method 8260B, the following QC verifications are required as part of the analytical sequence

- ❑ BFB Instrument Tune
- ❑ Initial Calibration/Initial Calibration Verification or Calibration Verification (SPCC/CCC evaluation)

Analytical sequences may be initiated by the analysis of a valid calibration verification (CV_I) in lieu of an initial calibration.
A complete definition and discussion of each of these internal QC samples is provided in the Laboratory Quality Management Plan.

12.0 Method Performance

12.1 Method development/Demonstration of capability. For this method, and all methods performed by LMP, Inc., these procedures must be completed as an initial demonstration of the ability to adequately perform this method.

12.2 Items specific to this method are as follows:

12.2.1 Method Detection Limits (MDLs). MDLs must be established for each target analyte by conducting an MDL study. This process is detailed in LMP's Determination of MDL/MQL/RL SOP. The following items are specific to this method:

- ❑ Water MDL. Prepare seven (7) laboratory control samples in reagent water at concentrations of 1.0, 5.0 and 20 µg/L. Analyze per the above SOP.
- ❑ Soil MDL Prepare seven (7) laboratory control samples in sodium sulfate at a concentration of 1.0 and 10.0 µg/Kg. Analyze per the above SOP.
- ❑ Soil Medium Level MDL. Prepare seven (7) laboratory control samples in sodium sulfate at a concentration of 100 and 500 µg/Kg. Analyze per the above SOP.
- ❑ Current MDLs for this method are listed in the Analyte Summary Table.

12.2.2 Demonstration of Capability (DOC). A DOC is required for each method prior to the use of this method on environmental samples, when there is a change in instrument type, personnel or test method. Refer to Employee Training SOP for a complete procedure. The following items are specific to this method:

- ❑ Water DOC. Prepare four (4) laboratory control samples in reagent water at a concentration of 100 µg/L.
- ❑ Soil DOC. Prepare four (4) laboratory control samples in sodium sulfate at a concentration of 100 µg/Kg.

13.0 Corrective Action for Outlier Conditions

13.1 Corrective actions for situations where certain acceptance criteria have not been met are provided in the Non-conformances and Corrective Action SOP Corrective action is included for many situations, including:

- ❑ BFB Tune
- ❑ Initial Calibration – ICAL
- ❑ Initial Calibration Verification - ICV
- ❑ Calibration Verification (Initial) – CVi
- ❑ Surrogate Recoveries
- ❑ Method Blank(s)
- ❑ Laboratory Control Sample(s)
- ❑ Matrix Spikes

14.0 Data Reduction, Assessment and Reporting

14.1 Procedures for the reduction, assessment and validation of data generated by the use of this method are detailed in LMP's Data Reduction and Review SOP.

15.0 Recordkeeping, Tracking and Archiving

15.1 Procedures for the keeping, tracking and archiving of information generated by the laboratory are detailed in LMP's Document Control Procedure SOP.

15.2 Items specific to this method are listed below.

- ❑ Initial Calibrations/ICVs
- ❑ Retention Time Window Studies

- ❑ Demonstration of Capability Studies
- ❑ Method Detection Limit Studies
- ❑ Reagent Logs
- ❑ Daily Run Logs
- ❑ Daily Analytical Sequences
- ❑ Raw Data – Extraction logs, Chromatograms, LIMS results

16.0 Preventive Maintenance

16.1 Preventive maintenance is a program designed to keep the performance of the instrument within acceptable working parameters. The instrument is routinely inspected, monitored and maintained in order to prevent costly down time.

16.2 Troubleshooting for the GC/MS is divided into discrete parts, allowing the analyst to independently assess the performance of each particular component.

16.3 The GC/MS system is currently maintained under service contract with Agilent Technologies. When service is needed, the vendor is phoned (800-227-9770) to open a service call.

16 4 When repairs are necessary, the equipment shall be taken out of service, repairs performed by either trained staff or trained service engineers.

16.5 A maintenance logbook is maintained for this instrument which keeps a detailed log documenting the preventive maintenance and repairs performed

17.0 Training and Training Validation

Policies and procedures for initial analyst training and follow-up verification of training are detailed in LMP's Employee Training SOP.

18.0 Waste Disposal and Pollution Management

Policies and procedures for waste disposal are detailed in LMP's Waste Management Plan SOP.

19.0 References

- ❑ LMP's Definitions, Acronyms, Symbols and Abbreviations Policy
- ❑ Method 8000B Solid Waste Manual SW-846 – Revision 2 December 1996
- ❑ Method 8260B Solid Waste Manual SW-846 – Revision 2 December 1996
- ❑ US Army Corps of Engineers – "Shell for Analytical Chemistry Requirements" EM 200-2-3, 1 Feb 01
- ❑ National Environmental Laboratory Accreditation Conference (NELAC) Quality Systems Chapter 5 Revision 15 May 25, 2001

Tables

Table 1

Equipment, Instrumentation and Apparatus

Item Description	Manufacturer	Cat #
0.5 µL Hamilton Syringe	Fisher	14-813-100
1.0 µL Hamilton Syringe	Fisher	14-824-20
5.0 µL Hamilton Syringe	Fisher	03-391-15E
10 µL Hamilton Syringe	Fisher	03-391-16E
Eppendorf Pipettor 10 µL to 100 µL	Fisher	05-402-48
Disposable Pasteur Pipets 5"	Fisher	13-648-6A
Gas Tight Syringe 10 mL	Fisher	14-823-16B
40 mL Septum Vials Clear	QEC	1112-40ML
40 mL Septum Vials Clear	QEC	1112-20ML
2 mL Amber Vial/Cap/Septa	Fisher	03-340-55D
2 mL Amber Vial Insert	Fisher	03-340-6B
Purge Trap K (3000)	Supelco	24920-U
Purge Trap K	Supelco	2-1066U
VOC System #1		**Status**
5890 GC w/ 5970 GC/MS	Hewlett Packard	Out of Service
VOC System #2		
Varian 3900 GC with Saturn 2100T GCMS	Varian	In Service
Encon	EST	
Purge & Trap Autosampler	Archon	
Column		
CP-7415 CP Select 624 CB DF =1.8 60m X 0.32mm ID		
VOC System #3		
5890 Series II GC w/ 5971 GC/MS	Hewlett Packard	In Service
LSC Purge & Trap 3000	Tekmar	
Purge & Trap Autosampler	Archon	
Column DB-VRX 50m X 0.25mm X 1.4µ		
VOC System #4		In Service
5890 Series II GC w/ 5971 GC/MS	Hewlett Packard	
LSC 2000 Purge & Trap	Tekmar	
Purge & Trap Autosampler	Archon	
Column DB-VRX 50m X 0.25mm X 1.4µ		

Table 2

Reagents/Solvents

Solvent	Grade	Manufacturer	Vendor/Cat #
Water	Organic Free	In-House Carbon Filter	
Methanol	Purge & Trap	Fisher	A4531
Sodium Bisulfate		Aldrich	307823
Hydrochloric Acid		LabChem	LC15130-3

Table 3

Certified Solutions

(All solutions provided in methanol unless otherwise indicated)

Standard ID	Vendor	Catalog #	Concentration
Surrogate	Accustandard	M-8240/60-SS-10X	2,000 µg/mL
Internal Standard	Accustandard	M-8260-IS-10X	2,000 µg/mL
Internal Standard/Surrogate	Accustandard	S-2978	2,000 µg/mL
BFB Tune	Accustandard	CLP-004-1000X	25,000 µg/mL
Matrix Spike	Accustandard	Refer to ICAL/CV	
Laboratory Control	Accustandard	Refer to ICAL/CV	
Calibration – ICAL/CV[1]			
Mix 1[2] Acrolein & Acrylonitrile	Accustandard	M-603-10X	10,000 µg/mL
Mix 2 Liquid Mix – Mod	Accustandard	M-502A-R2-10X	2,000 µg/mL
Mix 3 Gases	Accustandard	M-502B-10X	2,000 µg/mL
Mix 4 Additions	AccuStandard	M-8260-ADD-10X	2,000 µg/mL
Mix 5 Appendix IX	Accustandard	M-8240C-R6	Varied
Mix 6 Custom VOC Mix	Accustandard	S-4306	2,000 µg/mL
Mix 7 LMP Stock Solution			
Hexane	Fisher	Neat	2000-4000 µg/mL
Propyl Acetate	Aldrich	Neat	2000-4000 µg/mL
Tetrahydrofuran	Aldrich	Neat	2000-4000 µg/mL
Furan	Aldrich	Neat	2000-4000 µg/mL

ICAL – Initial Calibration
CV – Calibration Verification
1 – CV solutions are ordered as a second source from the ICAL solutions.
2 – Solution provided in water

Table 4

Intermediate Solution Dilution Schedule

Solutions listed here are made as intermediate solutions to be used in the preparation of a working standard for instrument calibration/verification or for spiking solutions, which will be added directly to samples during preparation. All solutions are prepared in methanol unless otherwise noted.

Standard ID	Catalog #	Volume	Final Volume	Concentration
Surrogate Mix	M-8240/60-SS-10X	1 mL	10 mL	200 µg/mL
Internal Standard Mix	M-8260-IS-10X	1 mL	4 mL	500 µg/mL
Internal Standards/Surrogates Mix	S-2978	1 mL	4 mL	500 µg/mL
BFB Tune	CLP-004-1000X	100 µL	50 mL	50 µg/mL
Mix 1 Acrolein & Acrylonitrile	M-603-10X	1 mL	5 mL	2,000 µg/mL
ICAL/CV Solution 1	ICAL/CV Solution 2	100 µL	10 mL	20 µg/mL
ICAL/CV Solution 2				
Mix 1 Acrolein & Acrylonitrile		1 mL	10 mL	200 µg/mL
Mix 2 Liquid Mix – Mod	M-502A-R2-10X	1 mL	10 mL	200 µg/mL
Mix 3 Gases[1]	M-502B-10X	1 mL	10 mL	200 µg/mL
Mix 4 Additions	M-8260-ADD-10X	1 mL	10 mL	200 µg/mL
Mix 5 Appendix IX	M-8240C-R6	1 mL	10 mL	200 µg/mL
Mix 6 Custom VOC Mix	S-4306	1 mL	10 mL	200 µg/mL
Mix 7 LMP Stock Solution		1 mL	10 mL	200 µg/mL – Aprox
Hexane	Neat			200 µg/mL – Aprox
Propyl Acetate	Neat			200 µg/mL – Aprox
Tetrahydrofuran	Neat			200 µg/mL – Aprox
Furan	Neat			200 µg/mL – Aprox

1 – This mix is prepared fresh weekly.

Table 5

Solution Spiking Levels

Solution ID	Matrix	Volume	Nominal Sample Size	Final Concentration
Internal Standard[1]	Water	1 µL	10 mL	50 µg/L
Internal Standard[1]	Soil	1 µL	5 g	50 µg/Kg
Internal Standard/Surrogate[1]	Water	1 µL	10 mL	50 µg/L
Internal Standard/Surrogate[1]	Soil	1 µL	5 g	50 µg/Kg
Laboratory Control[2]	Water	5 µL	10 mL	100 µg/L
Laboratory Control[2]	Soil	2.5 µL	5 g	100 µg/Kg
Matrix Spike[2]	Water	5 µL	10 mL	100 µg/L
Matrix Spike[2]	Soil	2 5 µL	5 g	100 µg/Kg

[1] – Solution added by Archon autosampler
[2] – ICAL/CV Solution 2: 200µg/mL

Table 6A

Working Standards Dilution Schedule – Targets and Surrogates

Aqueous Calibration

(All standards diluted into water)

Solution ID	Standard	Volume	Final Volume	Concentration
ICAL/CV Solution 1	WS-1	0.25 µL	10 mL	0.5 µg/L
Surrogate Mix	WS-1	0.25 µL	10 mL	5 µg/L
ICAL/CV Solution 1	WS-2	0.5 µL	10 mL	1 µg/L
Surrogate Mix	WS-2	0.5 µL	10 mL	10 µg/L
ICAL/CV Solution 1	WS-3	2.5 µL	10 mL	5 µg/L
Surrogate Mix	WS-3	1.0 µL	10 mL	20 µg/L
ICAL/CV Solution 2	WS-4	1.0 µL	10 mL	20 µg/L
Surrogate Mix	WS-4	1.5 µL	10 mL	30 µg/L
ICAL/CV Solution 2	WS-5	2.5 µL	10 mL	50 µg/L
Surrogate Mix	WS-5	2.0 µL	10 mL	40 µg/L
ICAL/CV Solution 2	WS-6	5.0 µL	10 mL	100 µg/L
Surrogate Mix	WS-6	2 5 µL	10 mL	50 µg/L
ICAL/CV Solution 2	WS-7	6.0 µL	10 mL	120 µg/L
Surrogate Mix	WS-7	3.0 µL	10 mL	60 µg/L
ICAL/CV Solution 2	WS-8	7.5 µL	10 mL	150 µg/L
Surrogate Mix	WS-8	3.5 µL	10 mL	70 µg/L
ICAL/CV Solution 2	WS-9	8.5 µL	10 mL	170 µg/L
Surrogate Mix	WS-9	4.0 µL	10 mL	80 µg/L
ICAL/CV Solution 2	WS-10	10 µL	10 mL	200 µg/L
Surrogate Mix	WS-10	4 5 µL	10 mL	90 µg/L

Standards are monitored by comparison to the initial calibration curve Fresh standards for the gases should be prepared if the CV exceeds 20%. Standards for gases will usually need to be replaced after one week. Other standards need to be replaced per the manufactures recommended expiration date or if comparison to the initial calibration indicates a problem.

ICAL/CV Solution 1 = 20µg/mL
ICAL/CV Solution 2 = 200µg/mL

Table 6B

Working Standards Dilution Schedule – Targets and Surrogates

Soil Calibration

(All standards diluted into water)

Solution ID	Standard	Volume	Final Volume	Concentration
ICAL/CV Solution 1	WS-1	0.25 µL	5.0 mL	1 µg/Kg
Surrogate Mix	WS-1	0.25 µL	5.0 mL	10 µg/Kg
ICAL/CV Solution 1	WS-2	0.5 µL	5.0 mL	2 µg/Kg
Surrogate Mix	WS-2	0.5 µL	5.0 mL	20 µg/Kg
ICAL/CV Solution 1	WS-3	2.5 µL	5.0 mL	10 µg/Kg
Surrogate Mix	WS-3	1.0 µL	5.0 mL	40 µg/Kg
ICAL/CV Solution 2	WS-4	1.0 µL	5.0 mL	40 µg/Kg
Surrogate Mix	WS-4	1.5 µL	5.0 mL	60 µg/Kg
ICAL/CV Solution 2	WS-5	2.5 µL	5.0 mL	100 µg/Kg
Surrogate Mix	WS-5	2 0 µL	5.0 mL	80 µg/Kg
ICAL/CV Solution 2	WS-6	5.0 µL	5.0 mL	200 µg/Kg
Surrogate Mix	WS-6	2.5 µL	5.0 mL	100 µg/Kg
ICAL/CV Solution 2	WS-7	6.0 µL	5.0 mL	240 µg/Kg
Surrogate Mix	WS-7	3.0 µL	5.0 mL	120 µg/Kg
ICAL/CV Solution 2	WS-8	7.5 µL	5.0 mL	300 µg/Kg
Surrogate Mix	WS-8	3.5 µL	5.0 mL	140 µg/Kg
ICAL/CV Solution 2	WS-9	8.5 µL	5.0 mL	240 µg/Kg
Surrogate Mix	WS-9	4 0 µL	5.0 mL	160 µg/Kg
ICAL/CV Solution 2	WS-10	10 µL	5.0 mL	400 µg/Kg
Surrogate Mix	WS-10	4.5 µL	5.0 mL	180 µg/Kg

Standards are monitored by comparison to the initial calibration curve. Fresh standards for the gases should be prepared if the CV exceeds 20%. Standards for gases will usually need to be replaced after one week Other standards need to be replaced per the manufactures recommended expiration date or if comparison to the initial calibration indicates a problem.

ICAL/CV Solution 1 = 20µg/mL
ICAL/CV Solution 2 = 200µg/mL

Table 7

GCMS System Configurations

GC/MS System 1
Out-of-Service

GC/MS System 2

Varian 3900GC	Saturn 2100 ION TRAP	Encon P & T	Archon ALS
MS Mass Range	35 – 260 amu		
MS Scan Time	0 47 secs/scan		
MS Source Temp	150 °C		
GC Injection Port	140°C	Split Flow Soil	
GC Detector Transfer Line	200°C		
GC Column	CP-Select 624		
GC Temp Program			
35°C	6 minutes	8°C/minute	
220°C	2 minutes	Runtime = 31 0minutes	
Tekmar Flow	40 mL/minute	11.0 minutes	
Tekmar Dry Purge	1.0 minute		
Tekmar Desorb	250°C	2 0 minutes	
Tekmar Bake	260°C	10 minutes	
Archon			

GC/MS System 3

HP 5890 Series II GC	HP 5971 MS	Tekmar 3000 P&T	Archon ALS
MS Mass Range	35 – 260 amu		
MS Scan Time	0.6 – 2 secs/scan		
MS Source Temp			
GC Injection Port	200°C	Split Flow	
GC Detector Transfer Line	280°C		
GC Column	DB-VRX	Flow	
GC Temp Program			
45oC	1 minutes	20°C/minute	
225oC	7 minutes	20°C/minute	
235oC	4 minutes	Runtime = 21 5 min	
Tekmar Flow	40 mL/minute	11.2 minutes	
Tekmar Dry Purge	2.0 minutes		
Tekmar Desorb	250°C	2.5 minutes	
Tekmar Bake	260°C	6 minutes	

Table 7 cont.

GCMS System Configurations

GC/MS System 4

HP 5890 Series II GC	HP 5971 MS	Tekmar 2000 P&T	Archon ALS
MS Mass Range	35 – 260 amu		
MS Scan Time	0.6 – 2 secs/scan		
MS Source Temp			
GC Injection Port	200°C	Split Flow	
GC Detector	280°C		
GC Column	DB-VRX	Flow	
GC Temp Program			
40oC	1 minutes	20°C/minute	
200oC	0 minutes	10°C/minute	
225oC	4 minutes	Runtime = 16.5 min	
Tekmar Flow	40 mL/minute	11.2 minutes	
Tekmar Dry Purge	2.0 minutes		
Tekmar Desorb	250°C	2.5 minutes	
Tekmar Bake	260°C	6 minutes	
Archon			

Table 8

BFB m/z Evaluation Criteria

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA*

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

* Alternate tuning criteria may be used, (e.g. CLP Method 624.2, or manufacturers' instructions) provided that method performance is not adversely affected.

Table 9

Summary Quality Objectives

Summary of Measurement quality objectives for Method 8260B Volatiles

Quality control element	Target Analyte / Surrogate	Poor Performance / Sporadic Marginal Failures[1]
Initial Calibration	Instrument Evaluation: SPCC's: minimum RF values per method requirement Evaluation: CCC's: verify %RSD 30%	No Allowance
	Primary Evaluation (all target analytes): r 0.995, %, RSD 15%, r^2 0.990	No Allowance
	Alternative Evaluation: Mean %RSD for all target analytes 15%, with maximum allowable restriction noted at right for individual analytes.	Alternative Evaluation: Maximum allowable %RSD for each individual target analyte 40%
ICV	% Rec = 80% - 120%	No Allowance
CCV	Instrument Evaluation. SPCC's: minimum RF values per method requirements	No Allowance
	Primary Evaluation (CCCs). %D 30% (USCOE: %D 20%)	No Allowance
MB	Target Analytes: Analytes < one-half MRL	Common Lab Contaminants: Analytes < MRL
LCS	Water & Solids: Refer to Analyte Summary Table	Sporadic Marginal Failures[1]: % Rec = 60% - 140%
MS	Water & Solids: Refer to Analyte Summary Table	Sporadic Marginal Failures[1]: % Rec = 60% - 140%
MSD/MD	Water: RPD 30% Solids: RPD No RPD limits	Water: RPD 40% Solids: No RPD Limits
Surrogates	% Interference-Free Matrix· Water & Solids: Refer to Analyte Summary Table	Sporadic Marginal Failures[1]: Water: % Rec = 15% - 150% Solids: % Rec - 20% - 150%

[1]The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported form the analysis. For instance, if the full list of target 68 compounds is reported from the GC/MS analysis, then 5 SMF's are allowed to the expanded criteria presented for the LCS. If the MS includes only a subset of compounds and for Surrogates, allow up to 1 SMF for this QC element

Appendix A

#1 - Notification Form of Method 5035
#2 - GC/MS Volatile Daily Run Log
#3 - GC/MS VOC Method 8260B Sequence Check List (SW-846
#4 - Initial Calibration (Form 6)
#5 - Characteristic Masses (m/z) for Purgeable Organic Compounds

Figure 1 - Notification Form of Method 5035

Date

Contact Name
Company
Address
City, State, Zip

Project Location:
Project Number:

Dear Mr. :
This has been generated to inform you of the fact that SW-846 Method 5030A for the analysis of volatiles in soil is no longer an approved method. This method has been deleted from SW-846 and has been replaced by SW-846 Method 5035.

While this method has been deleted from the Solid Waste Manual, it continues to be recognized and required by various state and government agencies.

The sole purpose of this letter is to document the notification of this method change and does not address the validity or acceptability of this method change.

Please call our laboratory if you have any questions.
Sincerely,

Nathan A. Pera
Project Manager

Client Notified [ ] Yes [ ] No Date notified: _____
Remarks: _____

Semivolatile Organic Compounds by GC/MS

Using SW-846 Method 8270C

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

1.1 This method is used to determine semi-volatile organic compounds in extracts prepared from a variety of waste matrices including ground water, soils, sediments and miscellaneous wastes.

1.2 Method 8270C can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride or 1:1 methylene chloride-acetone and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 of this SOP from SW-846 Method 8270C for a list of compounds and their characteristic ions.

1.3 The following compounds may require special treatment when being determined by this method:

1.3.1 Benzidine may be subject to oxidative losses during solvent concentration, and poor chromatographic peak shape.

1.3.2 Under the alkaline conditions of the extraction step, a-BHC, g-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.

1.3.3 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.3.4 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

1.3.5 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.

1.3.6 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material. Injection port maintenance is critical in maintaining response for these compounds.

1.3.7 Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. Additional verification standards need to be analyzed when modifying the injection port temperature as the performance of other analytes may be adversely affected.

1.4 LMP, Inc. reporting limits are based on project specific requirements. Reporting limits are based on the following (#1 being the default) :

1. The lowest point in the Initial Calibration Curve for a particular analyte (PQL)
2. Method Detection Limit factored for the appropriate matrix and sample size (SQL).
3. The lowest calibration standard that is no lower than 10 times the standard deviation as determined in the MDL study (MQL)

- PQL - Practical Quantitation Limit
- SQL - Sample Quantitation Limit
- MQL - Method Quantitation Limit

1.5 Appendix A #5 contains a recent Initial Calibration that shows the current list of Target Analytes for this method.

2.0 Summary of Method

2.1 Samples are to be prepared using one of the following sample preparation methods:

Method	Matrix	Extraction	LMP SOP
3510C	Water	Liquid/Liquid	Separatory Funnel Liquid-Liquid Extraction Method 3510C
3540C	Solid	Soxhlet	Soxhlet Extraction Method 3540C
3550B	Solid	Ultrasonic Extraction	Ultrasonic Extraction Method 3550B
3580A	Misc. Waste	Waste Dilution	Waste Dilution Method 3580A

2.2 Identification of target analytes is accomplished by comparing their Retention Time and Mass Spectra with the spectra of standards analyzed under the same conditions as the samples. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard with a minimum five-point calibration curve.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts of interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and solvents may be necessary.

3.1.1 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3 1 2 Glassware contamination can result in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem. Chromic acid that is not completely rinsed will cause similar problems with analyte degradation and should be carefully rinsed to avoid this problem. Refer to Organic Laboratory Glassware Cleaning SOP

3 2 The most common source of interference is from the solvents and reagents used during the preparation steps Reagent and solvent purity must continually be monitored through the extraction and analysis of Method Blanks

3.2.1 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of a solvent blank to check for cross contamination.

If cross-contamination is a potential and samples following a high level sample are positive for Target Analytes, these samples should be reviewed for possible cross-contamination. Baking out the column between analyses may eliminate some contamination. Changing the injector liner will also reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination or noted degradation in system performance.

3.2.2 High concentration samples present additional problems within the extraction lab Glassware must be scrupulously cleaned in order to prevent cross-contamination Organic Laboratory Glassware Cleaning SOP must be followed.

3.2.3 Carrier/Purge Gas - Zero Grade Helium

In order to minimize problems associated with contaminated high pressure tanks, the following precaution must be taken

- Each system must have a dedicated high-pressure tank and regulator This isolates each system and minimizes the chance of a single tank affecting more than one(1) instrument.
- LMP, Inc. has negotiated with our gas supplier, NexAir, to provide ultra clean, aluminum tanks. These tanks are individually labeled and are only used by LMP, Inc. In addition, a check valve is installed in each tank that will not allow use below 300 PSI.
- The analytical baseline is to be monitored daily for the presence of hydrocarbons which may indicate potential gas contamination. The high-pressure tank is to be replaced and returned to NexAir at the first sign of contamination.

4.0 Equipment and Apparatus

4.1 Glassware. Volumetric flasks, Class A (assorted sizes)

4.2 Miscellaneous. Eppendorf pipette, µL syringes (assorted sizes).

4.3 Equipment: Table 2 lists the current analytical systems and conditions.

4 3 1 Instrument/Equipment #1

4.3.1.1 Instrument Maintenance Schedule and Requirements

4.3.1.2 Maintenance Logbook

4.3.1.3 Daily Maintenance

4.3.1.4 Weekly Maintenance
4.3.1.5 Monthly Maintenance (Refer to Table 6, Maintenance Checklist)

4.4 A ChemStation for data acquisition controls each instrument. Raw data is uploaded to the NT Target Server for processing using Target and Envision software. A EPA/NIST Mass Spectral Library is available for the reporting of Tentatively Identified Compounds when requested by the client.

4.5 Mass spectrometers are each capable of scanning from 35 to 500 amu every 2 sec or less. The mass spectrometer is be capable of producing a mass spectrum for Decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 4 when 50 ng or less of the GC/MS tuning standard (DFTPP) is injected through the GC Refer to Table 2.

4.6 Volumetric flasks - Class A - Appropriate sizes with ground-glass stoppers.

4.7 Volumetric Pipettes - various volumes used for dilution.

4.8 Analytical Balance capable of weighing 0.0001g.

4.9 Bottles - Amber glass with Teflon lined screw caps.

4.10 Autosampler syringes: 5µL and 10µL Hamilton or equivalent

4.11 Volumetric Pipettes - Class A, various volumes used for dilution.

5.0 Reagents and Standards

5.1 Policy.

5.1.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.1.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Program (SVQAP).

5.2 Solutions and Standards are listed here at times using generic labeling (e.g., WS-1, ISTD1) to allow the analyst to follow the preparation of solutions. All solutions and standards will be uniquely identified and labeled as detailed in the following sections.

5.3 All reagents/solvents/standards must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Refer to Table 3A for a list of current solvents and reagents used.

5.4 All standards should be purchased as Certified Solutions

5.5 When a Certified Solution is not available, then the analyst must prepare the stock solution from a reference material of known purity using the procedures detailed in the Reagent and Standard Solutions Validation Program.

5.6 Secondary dilution standards - Using stock standard solutions, prepared in the appropriate organic solvent, secondary dilution standards containing the compounds of interest, either singly or mixed together.

5.7 Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. These standards can be stored for 6 months unless comparison to previous standards indicates potential degradation.

5.8 Stock Certified Solutions - These solutions are purchased as Certified Solutions from an outside source. Each solution is accompanied by certification data on the purity, precision, and traceability of the solution. Table 3B lists the currently used Certified Solutions for this method.

5.9 Stock Standard Solutions - Some standards may be prepared in-house using procedures as detailed in SOP Reagent and Standard Solutions Validation.

5.10 Internal Standard Solution (e.g., ISTD1) - This standard is added at the same volume to all standards and samples (QC and environmental). Internal standards used are 1,4-Dichlorobenzene-d(4), naphthalene-d(8), acenaphthene-d(10), phenanthrene-d(10), chrysene-d(12) and perylene-d(12). Table 3B lists the current solution.

5.11 GC/MS Tuning Standard (e.g., DFTPP1. .) - This standard contains 50ng/µL of Decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol and benzidine to verify tune criteria, injection port inertness and GC column performance. Table 3B lists the current solution

5.12 Calibration Standards (e.g., WS-1, WS-2) - A minimum five calibration standards (per analyte) at five difference concentrations. At least one standard should correspond to a sample concentration at or below that necessary to meet project data quality objectives. The remaining standards should encompass the working range of the GC/MS system. All quantitatively reported analytes must be included in the calibration standards. Table 3E details the Working Standards currently used. Surrogate standards are included in the calibration standards.

5.13 Surrogate Standards (e.g., BNS1, AES1) - These solutions are added to all *samples* prior to preparation. Surrogate Standard preparation is listed in Table 3C. The surrogates used in this method are phenol-d(6), 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d(5), 2-fluorobiphenyl and p-Terphenyl-d(14). Surrogate Standard spiking volumes and concentrations are listed in Table 3D.

5 14 Laboratory Control Solution (e.g., BNLCS1, AELCS1) - This standard contains all target analytes of interest for samples in a particular extraction batch and is added to a clean matrix (i e. Blank Spike) to monitor overall method performance. Laboratory Control Standard preparation is listed in Table 3C. Spiking volumes and concentrations are listed in Table 3D.

5.15 Matrix Spike Solution (e.g., BNMS1, AEMS1) - This solution contains all target analytes of interest for samples in a particular extraction batch and is added to aliquots of sample (MS/MSD) to monitor sample matrix effects. Matrix Spike Solution preparation is listed in Table 3C. Spiking volumes and concentrations are listed in Table 3D.

***Note*: The Organic Instrument Lab analyst prepares all spiking solutions used in the Organic Prep Lab. All solutions are documented in the Organic Instrument Lab Reagent Reference Log and Standard Reagent Log.**

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements. LMP's Sample Login Procedures SOP for container, preservation, and storage protocols

6.2 Holding Times

6.2.1 Holding Time for extraction is defined as the number of days from ***Sample Collection*** (e.g. Sample Date) to extraction.

6 2 2 Holding Time for analysis is defined as the number of days from ***Sample Extraction*** in the laboratory to date injected/analyzed by the instrument.

6 3 Store sample extracts at -10°C, protected from light, in sealed Teflon lined autosampler vials

7.0 Procedure

7.1 Samples are extracted prior to GC/MS analysis using one of the methods listed in Section 2.0:

7.2 GC/MS System Operating Conditions

7.2.1 Operating conditions for the Semi-Volatile systems are provided in Table 2

7.2.2 Injection port maintenance is performed on a daily basis prior to beginning the analytical sequence. All maintenance performed is documented in the appropriate system Maintenance Log.

- ❑ Replace injection port liner.
- ❑ Replace injection port seal.
- ❑ Replace injection port septa.
- ❑ Clip approximately 1 to 2 inches of column/guard column.
- ❑ This step can potentially cause a shift in retention times.
- ❑ The System Tune Standard must be monitored for any shift in retention times.
- ❑ Change all autosampler rinse solvent reservoirs.
- ❑ Bake GC at 325°C for a minimum of 1 hour.

Injection port maintenance should be performed as early in the morning as possible to allow the GC to bake for as long as possible prior to beginning the analytical sequence.

7.3 GC/MS System Tune

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 1 for a 50 ng injection of DFTPP1 (1µL injection of the DFTPP standard). The following approaches may be used to evaluate the DFTPP peak against the criteria in Table 4 :

7.3.2 A single scan may be taken (within 3 scans on either side of the apex) and evaluated

7.3.3 Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

7.3.4 Use the DFTPP mass intensity criteria in Table 4 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g. CLP, Method 525, or manufacturer's instructions), provided that method performance is not adversely affected.

All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions (DFTPP Tune File).

Analyses must not begin until tune criteria are met. The Target software will evaluate the DFTPP Spectra. Minor adjustments may need to be made to the acquisition DFTPP Tune File or as an option, the analyst may run Target Tune for DFTPP to help properly configure the Tune File. Only the Laboratory Supervisor may perform adjustments to the Tune File.

7.3.5 The GC/MS tuning standard solution is also used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. (See Sec. 8 0 of Method 8081 for the percent breakdown calculation). Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. The Target software calculates peak tailing factors and breakdown. The acceptance criteria for the peak tailing factor for Benzidine is <3.0 and Pentachlorophenol is <5.0.

7.3.6 If degradation is excessive and/or poor chromatography is noted, then additional injection port maintenance is required. It may also be necessary to break off the first 6-12 in. of the capillary column/guard column.

7.4 Initial Calibration

7.5 Prior to Initial Calibration, it is highly recommended that full system maintenance be performed. This includes venting the system and a complete source cleaning.

7.6 Performing Initial Calibrations is an expensive and vital procedure. If the system is not operating properly for the analysis of standards, it will not be possible to generate quality data during the analysis of samples. Make sure the analytical system is optimized prior to Initial Calibration.

7.6.1 Inject 1µL of WS-7 (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each Target Analyte. If interferences are noted, use the next most intense ion as the quantitation ion.

7.6.1.1 At this time, the WS-7 standard should be processed against the most recent ChemServer BNA method prior to the analysis of all Working Standards. (This level will be used for daily calibration verification.) This standard should be quantitated as a sample that includes spectral graphics for all Target Analytes.

This quantitative/qualitative report should be reviewed for:

a. False Negatives - If the method does not detect all Target Analytes in this standard, the method needs to be adjusted. (Check expected retention times, retention time windows, qualifier ion ratios).

b. False Positives - Review the quant report to ensure that all analytes have been correctly identified particularly those that are structural isomers.

c. Shifts in expected retention times. The quant report shows a Delta RT for all analytes. Evaluate any major shifts.

d. Spectral Quality - Due to the large number of Target Analytes, spectral overlap is a possibility, particularly as a column ages. Analyte spectra should be compared to NBS library spectra as a means of identifying overlap. The spectrum from WS-7 should be reviewed for use as the method reference mass spectrum in the qualitative analysis.

e. Compare response to previous calibrations. Pay particular attention to the SPCCs and CCCs.

f. Review general chromatography.

Initial Calibration is not to proceed until the analyst feels confident that the instrument/method will perform as expected. Any questions or concerns should be addressed to the Section Supervisor.

7.6.1.2 Inject 1µL of WS-1 (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each Target Analyte. This standard represents the lowest possible reporting limit (PQL). This standard is quantitated as a standard using a summary report

This quantitative/qualitative report should be reviewed for:

a. False Negatives - If the method does not detect all Target Analytes in this standard, the method needs to be adjusted.(Check expected retention times, retention time windows, qualifier ion ratios).

b False Positives - Review the quant report to ensure that all analytes have been correctly identified particularly those that are structural isomers.

Initial Calibration is not to proceed until the analyst feels confident that the instrument/method will perform as expected. Any questions or concerns should be addressed to the Section Supervisor.

If acceptance criteria have been met, the analyst may now analyze the full range of working standards.

7 6 2 Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. The RF is calculated as follows:

7.6.3

$$RF = (A(x)C(is))/(A(is)C(x))$$

where:

A(x) = Area of the characteristic ion for the compound being measured.

A(is)= Area of the characteristic ion for the specific internal standard

C(is)= Concentration of the specific internal standard.

C(x) = Concentration of the compound being measured.

The Target Software will calculate and generate an Initial Calibration Report which will summarize the Response Factors and %RSD for each of the Target Analytes.

7.6.4 System Performance Check Compounds - SPCCs

A system performance check must be made before the calibration curve is validated The SPCCs are used to check compound instability and to monitor for degradation caused by contaminated lines or active sites in the system.

The Response Factor for the SPCCs must meet the following criteria.

SPCC	Minimum RF
N-Nitroso-di-n-propylamine	0 050
Hexachlorocyclopentadiene	0.050
2,4-Dinitrophenol	0.050
4-Nitrophenol	0 050

These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate They are usually the first to show poor performance. Therefore, they ***must meet the minimum requirement*** in order to validate the Initial Calibration.

If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. ***This check must be met before sample analysis begins.***

7.6.5 Calibration Check Compounds - CCCs

7.6 5 1 The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column.

7.6.5.2 Using the RRFs from the initial calibration, calculate and record the percent relative standard deviation (%RSD) for all compounds. %RSD is calculated as follows:

$$\text{mean RF} \quad \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

RFi = RF for each of the calibration standards
RF = mean RF for each compound from the initial calibration
n = number of calibration standards

7.6.5.3 The RSD for each CCC must be less than or equal to 30%. The CCCs are as follows :

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
N-Nitrosodiphenylamine	Pentachlorophenol
Di-n-octyl phthalate	2,4,6-Trichlorophenol
Fluoranthene	
Benzo(a)pyrene	

If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Injection port maintenance should be performed, the system re-evaluated and re-calibration performed.

7.6.5.4 The RSD for all other analytes must be less than or equal to 15% to use the average RF Calibration options for those analytes with %RSD greater than 15% are listed below

7.6.5.5 Method 8000, Section 7.0 details several calibration options for analytes with %RSD > 15%.

Option 1: Review the results (area counts, calibration or response factors, and RSD) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be re-analyzed and the RSD recalculated. Replacing the standard may be necessary in some cases.

Option 2: Narrow the calibration range by eliminating one or more of low/high calibration standards. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

Note: The method quantitation limit is established by the concentration of the lowest standard analyzed during the initial calibration. Hence, narrowing the calibration range by changing the concentration of the lowest standard will, by definition, change the method quantitation limit. When the purpose of the analysis is to demonstrate compliance with a specific regulatory limit or action level, the analyst must ensure that the method quantitation limit is at least as low as the regulatory limit or action level.

Option 3: If the RSD of the calibration or response factors is greater than 15% over the calibration range, then linearity through the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that ***does not force through the origin***. This approach may also be employed based on past experience of the instrument response. This is most easily achieved by performing a linear regression of the instrument response versus the concentration of the standards. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x) This is a statistical requirement and is not simply a graphical convention.

The analyst should not force the line through the origin, but have the intercept calculated from the data points. In addition, do not include the origin (0,0) as a calibration point. The use of a linear regression may not be used as a rationale for reporting results below the calibration range demonstrated by the analysis of the standards. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. ***In order to be used for quantitative purposes, r^2 must be greater than or equal to 0.990.***

The curve may also be used, employing a quadratic response. R^2 must be greater than or equal to 0.995. Historically, typical semi-volatile analyses performed have met the 15% RSD or 0.995 criteria. If the Initial Calibration for these typical analytes cannot be met, that means that there is a problem with the instrument and corrective action must be taken prior to re-calibration.

7.6 5 6 The Target Software will calculate and generate an Initial Calibration Report that will summarize the Response Factors, %RSDs and/or r values as applicable for each of the Target Analytes.

7.6.5.7 Initial Calibration Report must be reviewed and signed by the analyst, and the Section Supervisor, and the QAO prior to the analysis of samples.

7.6.5.8 Initial Calibration Verification (ICV)

The ICV is a mid-range standard containing all target analytes, prepared form a source other than the initial calibration standards. The ICV must meet DCVS criteria, prior to the analysis of samples. The ICV is usually analyzed immediately following an initial calibration.

7.7 Calibration Verification

Calibration verification consists of several steps that are performed at the beginning of each 12-hour analytical shift. Acceptance criteria must be met prior to the analysis of any samples.

7.7.1 Perform injection port maintenance as per Section 7.2.2.

7.7.2 Perform GC/MS Tune as in Section 7.3

7.7.3 Analyze Daily Calibration Verification Standard (DCVS). Analyze standard WS-7 (50 ng/µL), used in the initial calibration.

7.7.4 Evaluate SPCCs for minimum RF of 0 050 as in Section 7.6.4. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. Re-analyze the DCVS These criteria must be met before sample analysis begins.

7.7.5 Evaluate CCCs listed in Section 7.6.5. Use percent difference when performing verification for average response factors.

$$\% \text{ Difference} = \frac{CF_v - \overline{CF}}{\overline{CF}} \times 100 \qquad \text{or} \qquad = \frac{RF_v - \overline{RF}}{\overline{RF}} \times 100$$

where CF and RF are the calibration factor and the response factor (whichever applies) from the analysis of the verification standard, and $\overline{CF}$ and $\overline{RF}$ are the mean calibration factor and mean response factor from the initial calibration.

7.7.6 The percent difference/drift for each CCC must be less than or equal to 20%. If the criterion is not met (i.e., greater than 20% difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project, then all analytes must meet the 20% difference or drift criterion.

7.7.7 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins

7.7.8 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required if necessary. (For example, re-analysis may not be required if the internal standard response is greater than 100% but the associated target analytes are not detected. This evaluation must be documented in the result package.)

7.7.9 For all other target analytes the % difference should be ≤30%. Certain reactive compounds (i.e., benzidine, benzoic acid) should be ≤35%.

7.8 GC/MS Analysis of Samples - GC/MS Analytical Sequence

7.8.1 A copy of the Extraction Log accompanies samples extracts from the Organic Prep Lab. The form is provided in Appendix A #3. Review this log for notes concerning anything encountered during extraction that may affect results or reporting limits (e.g., initial sample size reduction, adjustment of final volume above 1.0mL, problems such as emulsions)

7.8.2 Review the daily Sample Tracking Reports for prioritizing sample analysis. Any questions concerning the tracking report should be directed to the Section Supervisor.

7.8.3 Assemble all relevant Extraction Logs and work sheets. Review the work sheets to ensure that all Target Analytes requested have a current, valid Initial Calibration. Review work sheets for required reporting limits and QC reporting requirements.

7.8.4 Analytical Sequences are now constructed per Appendix A #1.

7.8.5 Allow the sample extract to warm to room temperature. Just prior to analysis, add 40 µL of the internal standard solution to the 1-mL concentrated sample extract.

7.8.6 Load the extracts onto the autosampler and start the sequence. The sequence begins with the analysis of the DFTPP Tune standard and the Daily Calibration Verification Standard. No sample analysis may begin until the acceptance criteria discussed under Section 7.7 has been met or Section 7.4 if this is an Initial Calibration.

7.8.7 Inject a 1µL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration (Section 7.4). The injection volume must be the same volume used for the calibration standards.

7.8.8 Upon completion of the sequence, the datafiles are transferred to the ChemServer to a temporary directory. At a ChemServer workstation, a new directory is created using the Sequence ID as the name of the directory. All relevant datafiles are then moved to this directory for automated processing.

7.8.9 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards.
Note: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution and anticipate the need for system inspection and/or maintenance.

7.8.10 All injections for the sequence must have been performed within the 12-Hour DFTPP tune window for data to be submitted as quantitative. Samples injected outside the 12-Hour tune window must be re-analyzed.

7.9 Qualitative analysis

7.9.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The laboratory using the conditions of this method must generate the reference mass spectrum. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds are identified when the following criteria are met.

7.9.1.1 Review of the quantitation report graphics should show good alignment of the quant ion with the qualifier ions Each should elute within one to two scans of each other. The Target method is set to encourage false positives to allow this graphical review.

7.9.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component. Review the Delta RT.

7.9.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20 % and 80 %.)

7.9.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights Otherwise, structural isomers are identified as isomeric pairs.

7.9.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.9.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.9.1.7 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification (TIC Report). The necessity to perform this type of identification will be determined by the report level (QC Level II, III or IV) requested by the client/project.

7.9.1.8 Tentatively Identified Compounds (TICs) are automatically reported during the ChemServer processing. If requested, the analyst must review these analytes for possible reporting as a TIC. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign or delete a tentative identification. Guidelines for tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 20% (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

- ❑ (3) Molecular ions present in the reference spectrum should be present in the sample spectrum.
- ❑ Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- ❑ Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. The standard Target quant report gives a background subtracted spectrum for each Target Analyte identified.
- ❑ The Target method assigns a Match Quality to all TIC hits. Any match quality below 50% should be considered highly suspect.
- ❑ After review of the TICs, any analytes not meeting the above criteria must be marked as not detected.

7.10 Quantitative Analysis

7.10.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.10.2 The concentration in the extract is determined using the average response factor or the linear regression equation from the initial calibration.

7.10.3 Where applicable, the concentration of any non-target analytes (TICs) identified in the sample should be estimated. This is performed by the Target software, using the closest internal standard.

7.10.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.10.5 Quantitation of multi-component compounds (e.g., Toxaphene, Aroclors, etc.) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD, by Methods 8081 or 8082. However, Method 8270 may be used to confirm the identification of these compounds, when the concentrations in the final extract are high enough

8.0 Quality Control/Quality Assurance/Corrective Action

8.1 Corrective Action – Corrective Action is the process by which problems within the laboratory are identified, proper personnel are notified, the problem solved or justified, correction implemented and the Corrective Action documented.

8.2 The quality control procedures detailed in this SOP are based on the Solid Waste Manual Update III Chapter One, Method 8000B and Method 8270C.

8.3 Quality control procedures for sample preparation are found in the appropriate extraction SOP. Refer to Section 2.1 for a listing.

8.4 The GC/MS system must be evaluated and meet all acceptance criteria as listed in Sections 7.3, 7.4 and 7.5 prior to the analysis of samples.

8.5 Samples must have been injected within the 12-Hour DFTPP tune window to be considered for quantitative reporting.

8.6 Initial Demonstration of Capability (IDC) - This demonstration is performed per matrix for each method of extraction (e.g., 3510, 3550…). The IDC is performed initially for any new method or when a major modification/revision is made to a current method. In addition, this IDC is performed to validate a new extraction technician.

A new analyst for GC/MS semi-volatiles is validated by the successful completion of an Initial Calibration, Calibration Verification and IDC.

8.6.1 Four (4) reference samples (Laboratory Control Samples) are prepared from a spiking solution containing each analyte of interest. The LCS concentrate (spiking solution) is purchased as a certified solution. Preparation of the LCS solution and extraction and analysis of the LCS are performed exactly like samples per the applicable extraction SOP using a clean matrix. A successful IDP is completed when recoveries for all Target Analytes fall within acceptance criteria for each of the four (4) controls.

8.7 Method Blank (MB) - Used to assess the general performance of the laboratory. Method blanks are analyzed to assess background interference or contamination that exists in the analytical system that might lead to the reporting of elevated concentration levels or false positive data. The method blank is defined as an interference-free blank matrix similar to the field sample matrix to which all reagents are added in the

same volumes or proportions as used in sample preparation and carried through the complete sample preparation, cleanup, and analytical procedures. For aqueous analyses, analyte-free reagent water would typically be used. For soil analyses, a purified solid matrix (e.g., sand or sodium sulfate) is used. At least one method blank shall be analyzed with each preparation batch of samples. Typically, the method blank would be analyzed before any of the other batch samples. The results of the method blank analysis are evaluated, in conjunction with other QC information, to determine the acceptability of the data generated for that batch of samples. Sample results shall not be corrected for blank contamination.

8.7.1 Analytes identified in the Method Blank that are also identified in environmental samples associated with that blank must be flagged as "B - Detected in Blank". Phthalates are the most common contaminant identified in semi-volatile method blanks. Reporting limits for these contaminants must be reviewed on a constant basis and revised as necessary to reflect accurate analytical conditions.

8 8 Laboratory Control Sample (LCS) - A laboratory control sample (LCS) must be processed with each batch of samples in order to assess whether the analytical procedures employed (in an interference-free matrix) are in control. All target analytes are be spiked into the LCS. The LCS undergoes the same preparatory and cleanup procedures as was used for the environmental samples.

8.8.1 Control limits for aqueous and solid matrices are generated for all target analytes and surrogates in the LCS.

8.8.2 If the LCS is out of control, corrective action must be taken. The source of the problem must be investigated and the effect on the samples must be evaluated For example, if an analyte in the LCS has a recovery above the upper acceptance limit, but the same analyte is not detected in any of the environmental samples in the batch or is detected at less than 5% of the action level, additional corrective measures may not be necessary. For all other situations, reanalyze the LCS extract to verify the out-of-control condition. If the LCS remains out of control, all the samples in the batch must be re-extracted and reanalyzed for the failed target analytes (i.e., the target analytes with unacceptable LCS recoveries)

8.8.3 LMP, Inc has adopted the following policy regarding LCS evaluation:

8.8.3 1 Sporadic Failures

A sporadic failure is defined as marginal failure due to random (as opposed to gross systematic) error Due to the number of target analytes present in the LCS, it is likely that sporadic failures will occur. Refer to Table 5.

For the scope of work under the U.S. Army Corps of Engineers, LMP, Inc will allow follow the sporadic failure rate as designated by Shell Document, EM 200-1-3 Table I-15:

Number of Allowable QC Failures

N	X
5-15	1
16-30	2
31-45	3
46-60	4
61-75	5
76-90	6
91-105	7

Note: N = number of reported method target analytes
X = sporadic marginal failure allowed

A sporadic failure does not require corrective action other than documentation and monitoring of the failure. A Case Narrative is also not necessarily required unless the failure has a direct impact on the reported data.

Classification of a flagged recovery as a sporadic failure requires approval from the Section Supervisor. Recoveries must be monitored on a continual basis to ensure that these failures are not analyte(s) dependent. If the sporadic failures are consistently with the phenolic compounds, then recoveries of all phenolic compounds should be reviewed to identify any potential trend

8.8.3.2 LCS Evaluation

- ❑ LCS recovery is high for an analyte not identified in any samples associated with the LCS. The data will be considered valid as the high recovery indicates that detection limits were not affected. The analyte(s) recovery should be monitored daily for a trend that might indicate the need for corrective action. No re-extraction/re-analysis required. Refer to Section 8.10.
- ❑ LCS recovery is high for an analyte identified in samples associated with the LCS. The LCS and sample(s) should be re-extracted/re-analyzed for the failing analyte only. If the LCS and sample(s) cannot be re-analyzed (e.g., holding time expired, no additional sample available…) then the final result must be flagged as "J - Estimated Value" and a Case Narrative provided detailing the exact recovery of the LCS.
- ❑ LCS recovery is low for an analyte identified in samples associated with the LCS. The LCS and sample(s) should be re-extracted/re-analyzed for the failing analyte only. If the LCS and sample(s) cannot be re-analyzed (e.g., holding time expired, no additional sample available…) then the final result must be flagged as "J - Estimated Value". A Case Narrative must be provided detailing the exact recovery of the LCS and that the reported value for the flagged analyte represents a minimum value.

8.8.4 Laboratory Control Sample Duplicates - LCSD

8.8.4.1 LCSDs are extracted under the following circumstances :

- ❑ Not enough sample available to perform both MS/MSD
- ❑ Only sample available for MS/MSD is a Field Blank or Equipment Rinsate. No MS/MSD is to be extracted on these type samples.
- ❑ Required by the project Sampling and Analytical Plan

8.8.4.2 RPD limits for LCS/LCSD should not exceed 20%.

8.8.4.3 If duplicate precision for the LCS is not in control, corrective action must be taken. However, if RPDs are outside of control limits, the batch need not be rejected (as long as the recoveries are acceptable).

8.9 Matrix Spikes (MS) - A Matrix Spike and Matrix Spike Duplicate should be processed with each batch of samples in order to assess the overall performance of the method as applied to a particular matrix.

8.9.1 Recoveries flagged as outside QC Limits for the MS/MSD should be evaluated for a potential matrix effect. LCS/LCSD recoveries must be within QC Limits for the failing analyte in order to be classified as a matrix effect.

- ❑ Review the chromatogram for obvious interferences
- ❑ High levels of Non-Target Analytes (e.g., hydrocarbons…) as indicated by the TIC report. TIC reports are to be provided for any sample that has failing MS/MSD recoveries.
- ❑ Chromatographic interference as indicated by a significant elevation in the baseline.
- ❑ Review the extraction log :
  - 1.Was initial pH, prior to extraction, noted as high or low?
  - 2.Were emulsions formed during liquid/liquid extraction?
  - 3.Was sample size reduced due to the potential for saturation?
  - 4.Was final volume adjusted due to the inability to concentrate to 1.0mL?
  - 5.Were problems during the extraction/concentration noted? (e.g., portion of extract spilled during transfer)

8.9.2 If review of the data shows apparent matrix interference or if site history indicates previous typical recoveries, no re-extract/re-analysis is necessary.

8.9.3 If no matrix interference is apparent, the laboratory must confirm the presence of matrix interference via the re-extraction and re-analysis of an the MS/MSD. The MS/MSD need only be analyzed for the failed target analytes. If the MS/MSD for the re-extraction/re-analysis is still outside of control limits (and matrix interference is not apparent) then the recovery data is qualified as due to matrix interference.

8.9.4 If the RPD acceptance criteria are not satisfied, and the recovery criteria are exceeded, then and only then, re-extract and analyze a second MSD for the failed analytes. Reanalyze the extract if there is insufficient sample. Calculate the %RSD for the set of three analyses (e.g., the MS, the first MSD, and the second MSD). If the %RSD for the set of 3 analyses is greater than one half the RPD QC

limit plus 5% (e.g.,30%), qualify all associated samples for poor precision A Case Narrative must be provided for Level III/Level IVM packages detailing the review and findings for the outlier MS/MSD recoveries.

8.9.5 RPD limits for MS/MSD should not exceed 20%.

8.10 Surrogates - Surrogates are used to assess the overall performance of the method as applied to a particular matrix on a sample-by-sample basis. Surrogates are evaluated in the same manner as the MS/MSD. Refer to Section 8.8.1 - 8.8.3.

9.0 Calculations

9 1 The Target data processing software performs calculations. Target calculations are verified against the following:

9 2 The concentration of each analyte in the sample is calculated using the results of the initial calibration, according to one of the following sections, depending on the sample matrix:

9.2.1 Aqueous samples - Internal Standard - Average RF

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(C_{is})(D)(V_t)}{(A_{is})(\overline{RF})(V_s)(1000)}$$

A_s = Area (or height) of the peak for the analyte in the sample.
V_t = Total volume of the concentrated extract (µL). For purge and trap analysis, V_t is not applicable and therefore is set at 1.
D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is dimensionless.
CF = Mean calibration factor from the initial calibration (area per ng).
V_t = Volume of the extract infected (µL). The nominal injection volume for samples and calibration standards must be the same. For purge and trap analysis, V_t is not applicable and therefore is set at 1. If concentration units are used in calculating the calibration factor, then V_t is not used in this equation.
V_s = Volume of the aqueous sample extracted or purged in mL. If units of liters are used for this term, then multiply the results by 1000

9.2.2 Non-Aqueous samples - Internal Standard - Average RF

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(C_{is})(D)(V_t)}{(A_{is})(\overline{RF})(W_s)(1000)}$$

where A_s, A_{is}, C_{is}, D and $\overline{RF}$ are the same as for aqueous samples, and

W_s = Weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term multiply the results by 1000.

The 1000 in the denominator represents the number of µL in 1 mL If the injection (V_t) is expressed in mL, then the 1000 may be omitted.

Using the units specified here for these terms will result in a concentration in units of ng/g which is equivalent to µg/kg.

7 10 2 3 If a linear calibration that does not pass through the origin has been employed then the regression equation is rearranged in a fashion similar to that described in Sec 7 10 1 3

9.2.3 If a linear calibration that does not pass through the origin has been employed, then the regression equation is rearranged as shown in Sec. 7.5.2, and the concentration of the analyte is calculated from the area response (y), the slope (a), and the intercept (b). When using this form of linear calibration, it is the laboratory's responsibility to ensure that the calculations take into account the volume or weight of the original sample, the dilution factor (if any), and dry weight (as applicable) One

approach to this calculation is to perform the original linear regression using the concentration of the analyte in the final extract volume or the volume purged. The concentration of the analyte in the sample may then be calculated as follows:

$$C_s = \frac{(C_{ex})(V_t)}{(V_s)}$$

where:

C = Concentration in the sample
C = Concentration in the final extract
V = Total volume of the concentrated extract
V = Volume of the sample extracted or purged
For solid samples, substitute the weight of the sample, W , for V .
For purge-and-trap analyses, the concentration of the analyte in the volume of the sample that is purged will be the same as in the original sample, except when dilutions are performed.

9.3 Unless otherwise specified, all semi-volatile soil results are reported at Dry Weight.

10.0 Data Validation

10.1 The analyst completes sequence Checklists for each analytical sequence. Refer to Appendix A #2. The analyst must complete the checklist and ensure that all method Quality Assurance requirements have been met.

10.2 Once the sequence has been reviewed, the analyst will complete any applicable QC Forms needed to summarize any Quality Control Samples analyzed.

- ❑ Surrogate Summary
- ❑ Method Blank Summary
- ❑ Laboratory Control Sample(s)
- ❑ Matrix Spike/Matrix Spike Duplicate

10.3 The analyst is required to complete, review, sign and date the work sheets prior to submission (Level I review).

10.4 The Section Supervisor (or designate) will then review the data package to ensure completeness and accuracy (Level II review). The Section Supervisor is ultimately responsible for the quality of the Level II review.

10.5 The Organic Laboratory Supervisor is responsible for ensuring that all work sheets, reagent logs, standard logs and maintenance logs are completed and up to date. Refer to the Data Reduction and Review SOP.

11.0 Waste Management

11.1 Refer to LMP Waste Management Plan

12.0 Health and Safety

12.1 The toxicity or carcinogenicity of reagents and standards used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals is to be reduced whenever possible. Material Safety Data Sheets are available and are maintained by the Quality Assurance Officer. Refer to the Chemical Hygiene Plan and Laboratory Safety Plan SOPs

13.0 Training & Training Validation

13.1 Employee training on documented procedures may be found in the Employee Training SOP.

13.2 Demonstration of the employee's training in the specific procedures involved in this method may be found in the Training Documents Log This documentation includes all in-house and outside training received and include items such as proficiency testing and information on performance testing results. A Demonstration of Capability is on file for each analyst performing the test.

14.0 References

- ❑ LMP's Definitions, Acronyms, Symbols and Abbreviations Policy

- Solid Waste Manual, SW846 Update III, December 1996.
- U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements EM 200-1-3, 1 Feb 01.
- EPA, Methods for Chemical Analysis of Water and Wastes, EPA –600/4-79-020, March 1983
- NELAC, Quality Systems, Revision 15, May 25, 2001.
- NELAC, Program Policy and Structure, Revision 13, June 29, 2000.
- 40 CFR Part 136 Appendix A.
- EPA Guidance for Preparing Standard Operating Procedures (SOPs), EPA QA/G-6, EPA/240/B-01/004, March 2001
- USEPA 2185 – Good Automated Laboratory Practices
- OSHA Laboratory Standard, 29 CFR 1910.1450.
- OSHA Compliance Guide, Kirk H. Ray, 8th Edition.
- *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.
- Laboratory Safety in Practice. A Comprehensive Compliance Program and Safety Manual.
- *"Safety in Academic Chemistry Laboratories"*, American Chemical Society Publication, Committee on Chemical Safety.
- *"Carcinogens – Working with Carcinogens"*, Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

Tables:

Table 2
Current Analytical Systems and Conditions

System 1 - BNA-1

HP 5973 Mass Selective Detector coupled with a HP 6890 capillary GC. The GC is equipped with a 100-place HP 7673 Autosampler.

Column - 30m x 0.25mm ID capillary column VF-5MS (Varian), 0.25µm film thickness
Initial Temp. 50°C Hold for 2 minutes
Temperature Program 1: 50°C/Minute to 280°C for 0 Minutes
Temperature Program 2: 40°C/Minute to 325°C for 1.5 Minutes

System 2 - BNA-2

HP 5971A Mass Selective Detector coupled with a HP 5890 II capillary GC. The GC is equipped with a 100-place HP 7673 Autosampler. The GC has a Restek GC Racer attached to aid with temperature increases.

Column - 30m x 0.25mm ID capillary column ZB-5 (Phenomenex), 0.25µm film thickness
Initial Temp: 50°C Hold for 2 minutes
Temperature Program 1: 25°C/Minute to 280°C for 0 Minutes
Temperature Program 2: 10°C/Minute to 325°C for 3 Minutes

System 3 - BNA-3

HP 5971 Mass Selective Detector coupled with a HP 5890 II capillary GC. The GC is equipped with a 100- place HP 7673 Autosampler.

Column - 30m x 0 25mm ID capillary column ZB-5 (Phenomenex), 0.25µm film thickness
Initial Temp: 50°C Hold for 2 minutes
Temperature Program 1 33°C/Minute to 280°C for 1 Minute
Temperature Program 2· 30°C/Minute to 325°C for 10.5 Minutes

Table 3A
Reagents/Solvents

Solvent	Grade	Manufacturer	Vendor/Cat #
Methylene Chloride	GC Grade	Fisher	D151-4
Methanol	Purge & Trap	Fisher	A454-4
Acetone	GC Grade	Fisher	A928-4

Table 3B
Certified Solutions

Standard ID	Vendor	Catalog #	Concentration µg/L
Base Neutral Surrogates Mix	ECS	ECS-N-002	1000
Acid Surrogates Mix	ECS	ECS-N-003	2000
Internal Standards	ECS	ECS-N-001	4000
DFTPP Tune	Accustandard	M-625-TS-20X	1000
BNA Calibration Standards			
Acid Composite Mixture	Accustandard	CLP-HC-A-R	2000
Base/Newtral Composite Mixture	Accustandard	CLP-HC-BN-R	2000[1]
Custom CLPHC Additions Mix	Accustandard	S-7027B-R1	2000
Composite Mix 2	Accustandard	Z-014E-R	2000
Benzidine and 3,3-dichlorobenzidine	Accustandard	Z-014F	2000[2]
Second Source Standards			
Acids Mix 3	Crescent	CC2471R	2000
Base/Neutral Mix 1	Crescent	CC2458	2000[3]
Semivolatiles Mix 5	Crescent	8SM-008	2000
Appendix IX Semivolatiles	Crescent	CC2289A	2000
Chlorobenzilate Solution	Crescent	7259D.20	2000
Semivolatile Mix with Pyridine and Carbozole	Crescent	CC2473	2000
Proposed Mixes			
DEP(MA)-PAH Mix (for PAH MS only)	Accustandard	DRH-0065	1000
Phthalates Esters (for PE MS only)	Accustandard	M-8060	2000[4]

All solutions in Methylene Chloride unless otherwise indicated.
[1] - Provided in Benzene. Methylene Chloride Acetonitrile (2:2.1)
[2] - Provided in Methanol
[3] - Provided in Benzene. Methylene Chloride
[4] - Provided in Isooctane.

Table 3C
Solution Dilution Schedule

Solutions

Solutions listed here are made as Intermediate Solutions to be used in the preparation of a Working Standard for instrument calibration/verification or for Spiking Solutions which will be added directly to *samples* during preparation.

Standard ID	Catalog #	Volume (mL)	Final Volume (mL)	Concentration	Solution ID
Internal Standards	ECS-N-001	5	20	1000 ng/uL	ISTD1
BN Surrogate Mix	ECS-N-002	10	100	100 µg/mLs	BNS1
AE Surrogate Mix	ECS-N-003	5	100	100 µg/mL	AES1
Full List Laboratory Control	All BNA Calibration Standards	0.5	100	10 µg/mL	LCSFL1
Acid Matrix Spike	CLP-HC-A-R	1	40	50 µg/mL	MSAE1
Phthalate Matrix Spike	M-8060	1	40	50 µg/mL	MSPhth1
PAH Matrix Spike	DRH-0065	1	40	50 µg/mL	MSPAH1

Table 3D
Solution Spiking Levels

Solution ID	Matrix	Volume	Nominal Sample Size	Final Concentration
Internal STD -ISTD1	Final Extract	40 µL	Not Applicable	Not Applicable
Surrogates - BNS1	Aqueous	1.0 mL	1000 mL	100 µg/L
Surrogates -AES1	Aqueous	1.0 mL	1000 mL	100 µg/L
Surrogates - BNS1	Solid	1.0 mL	30 g	3,333 µg/Kg
Surrogates - AES1	Solid	1.0 mL	30 g	3,333 µg/Kg
Lab Control - LCSFL1	Aqueous	5.0 mL	1000 mL	50 µg/L
Lab Control - LCSBN1	Solid	5.0 mL	30 g	1,667 µg/Kg
Acid Matrix Spike - MSAE1	Aqueous	1.0 mL	1000 mL	50 µg/L
Acid Matrix Spike - MSAE1	Solid	1.0 mL	30 g	1,667 µg/Kg
Phthalate Matrix Spike - MSPhth1	Aqueous	1.0 mL	1000 mL	50 µg/L
Phthalate Matrix Spike - MSPhth1	Solid	1.0 mL	30 g	1,667 µg/Kg
PAH Matrix Spike - MSPAH1	Aqueous	2 0 mL	1000 mL	50 µg/L
PAH Matrix Spike - MSPAH1	Solid	2 0 mL	30 g	1,667 µg/Kg

Final concentration is to be adjusted for actual sample size.

Table 3E
Standards Dilution Schedule

Solution ID	Standard ID	Volume	Final Volume	Concentration
DFTPP Tune (DFTPP1)	M-625-TS-20X	1 mL	20 mL	50 ng/µL
Initial Calibration Standards (ICAL)				
WS-1[2]	WS - 9	2 µL	1 mL	0.2 ng/µL
WS-2[2]	WS - 9	5 µL	1 mL	0.5 ng/µL
WS-3[2]	WS - 9	20 µL	1 mL	2.0 ng/µL
WS-4[2]	WS - 9	50 µL	1 mL	5 0 ng/µL
WS-5[2]	WS - 9	100 µL	1 mL	10.0 ng/µL
WS-6[2]	WS - 9	200 µL	1 mL	20.0 ng/µL
WS-7[1]	All BNA Calibration Standards and Surrogates	50 µL, except 100 µL for Base Surrogates	2 mL	50.0 ng/µL
WS-8[2]	All BNA Calibration Standards and Surrogates	40 µL, except 80 µL for Base Surrogates	1 mL	80.0 ng/µL
WS-9[1]	All BNA Calibration Standards and Surrogates	100 µL, except 200 µL for Base Surrogates	2 mL	100 ng/µL
WS-10[2]	All BNA Calibration Standards and Surrogates	60 µL, except 120 µL for Base Surrogates	1 mL	120 ng/µL
WS-11[2]	All BNA Calibration Standards and Surrogates	80 µL, except 160 µL for Base Surrogates	1 mL	160 ng/µL
Second Source Calibration Verification				
ICV[1]	All 2nd Source Standards + Z-014F and Surrogates	50 µL, except 100 µL for Base Surrogates	2 mL	50.0 ng/µL

All standard solutions diluted into Methylene Chloride unless otherwise indicated.

[1] - Add 80µL of ISTD1
[2] - Add 40µL of ISTD1

Table 4
DFTPP Key Ions and Ion Abundance Criteria

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a,b]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

[a] Data taken from Reference 3
[b] Alternate tuning criteria may be used, (e.g., CLP, Method 525, or manufacturers' instructions) provided that method performance is not adversely affected

Table 5

Summary of Measurement quality objectives for Method 8270C Semi-volatiles

Quality control element	Target Analyte / Surrogate	Poor Performance / Sporadic Marginal Failures[1]
Initial Calibration	Instrument Evaluation: SPCC's: minimum RF values per method requirement Evaluation: CCC's: verify %RSD 30%	No Allowance
	Primary Evaluation (all target analytes): r 0.995, %, RSD 15%, r^2 0.995	No Allowance
ICV	Instrument Evaluation: SPCC's: minimum RF values per method requirements	No Allowance
	Primary Evaluation (CCCs)· %D 20%	No Allowance
	All Additional Analytes 30%	Poor Performers. 35%
CCV	Same as ICV	
MB	Target Analytes: Analytes < one-half MRL	Common Lab Contaminants: Analytes < MRL
LCS	Water & Solids: See Analyte Summary Table	Sporadic Marginal Failures[1]: Water: % Rec = 15% - 150% Solids: % Rec = 25% - 150%
MS	Water & Solids: See Analyte Summary Table	Sporadic Marginal Failures[1]· Water: % Rec = 15% - 150% Solids: % Rec - 20% - 150%
MSD/MD	Water & Solids. RPD 20%	Sporadic Marginal Failures[1]: Water: RPD 60^ Solids: RPD 60^
Surrogates	% Interference-Free Matrix[2]: Water & Solids: See Analyte Summary Table	Sporadic Marginal Failures[1]: Water: % Rec = 15% - 150% Solids: % Rec - 20% - 150%

[1]The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported form the analysis. For instance, if the full list of target compounds is reported, then 5 SMF's are allowed to the expanded criteria presented for the LCS. If the MS includes only a subset of compounds and for Surrogates, allow up to 1 SMF.
[2]B = base, N = neutral, A = acid compounds (cmpds)

Appendix A

#1 Analytical Sequence

#2 Semi-Volatile Sequence Check List

#3 Organic Prep Lab Extraction Log

#4 Daily Run Log

#5 Initial Calibration (Form 6)

#1 Analytical Sequence

1.0 The analyst is required to complete the Daily Run Log anytime analysis is performed on an analytical system. Each log is specific to a particular system. See example log in Appendix A #4.
The information entered in this log will be used to create the analytical sequence on the system ChemStation.

1.1 Date of Analysis - Date of first injection of the sequence.
1.2 Method - 8270C, 625, combinations
1.3 System ID
1.4 Sequence ID - Name using the following format :

B(SysID)MMDD(Seq#)
(e.g., B2040101)

B		(BNA Analysis - 1 Character)
SysID -	1, 2 or 3	(System ID - 1 Numeric)
MMDD -	Today's Date	(Month Day)
Seq# -	Sequence #	(01 for first sequence, 02 for second sequence, etc.)

1.5 Slot # - Autosampler tray slot that extract vial is located. (#1 thru #100)
1.6 Sample ID -LMP, Inc. LIMS assigned ID (9804-001-02)
1.7 SS- Sample Size (from extraction log)
1.8 D - Dilution Factor
1.9 Client Name
1.10 Batch # - Extraction Batch (from extraction log)
1.11 Comments
1.12 Time of analysis

2.0 Based on the above log, the analyst will assemble and prepare extracts (i.e., add internal standard, perform dilutions...). These extracts are then loaded onto the autosampler in the appropriate slot. The next step is to complete the ChemStation
sequence. Information entered in this sequence will be transferred directly to the ChemServer for processing.
A typical sequence is as follows :

Starting sequence Tue Apr 21 15:49:54 1998
Sequence Name: C:\HPCHEM\1\SEQUENCE\B2042101.S
Comment:
Operator: MK
Data Path: C:\HPCHEM\1\DATA\b2042101\
Method Path: C:\HPCHEM\1\METHODS\

Line Type	Vial	DataFile	Method	Sample Name
1) Sample	2	0201001	DFTPP	DFTPP
2) Sample	3	0301002	B20728B	,DCS BNA 50,1,1,1,,0,,,
3) Sample	4	1401013	B20728B	9804-554,9804-554-1,2,1,0,,0,30.6
4) Sample	5	1501014	B20728B	9804-554,9804-554-1MS,2,1,3,MS,1,
5) Sample	6	1601015	B20728B	9804-554,9804-554-1MSD,2,1,3,MSD,
6) Sample	7	1701016	B20728B	9804-554,9804-554-2,2,1,0,,0,30.4
7) Sample	8	1801017	B20728B	9804-486,9804-486-2,2,1,0,,0,30.3

#1 Analytical Sequence (cont.)

2.1 Sample information is entered in the same order as the Daily Run Log.
2.2 The Vial and DataFile entries are created automatically by the ChemStation
2.3 Method is the analytical method on the ChemStation for data acquisition only. The quantitation method is stored on the ChemServer.
2.4 Sample Name includes data that will be used by the ChemServer during.
2.5 Sample Definition Information
Ensures that data station header information is translated properly to Target.

DataFiles: All entries are separated by Commas.

Variable	Definition	Example
ClientSDG	Client Sample Delivery Group (LIMS Order #)	9804-010
ClientSmpID	Client Sample ID (LIMS Order #)	9804-010-1
SmpMatrixType	Sample Matrix 0=gas 1=liquid 2=solid 3=none	2
DilFactor	Dilution Factor	10
SampleType	0=unknown 1=calib 2=cont calib 3=QC sample	3
QCType	MS/MSD LCS/LCSD	MS
SpikeSample	Perform spike recovery calc 0=no 1=yes	1
WS	Sample Size g/mL	5
LabPrepBatch	Prep-Lab Extraction Page #	V15BTXSO41

Organochlorine Pesticides by GC According to SW-846 Method 8081A

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

1.1 This method is used to determine the concentration of various chlorinated pesticides. This SOP addresses the requirements of SW-846 methods 8000B (Revision 2 December 1996) and 8081A (Revision 1 December 1996) This method is applicable to the analysis of water, soil, liquid and solid samples.

1.2 Instrumentation: Dual capillary GC equipped with dual electron capture detectors (ECD) and autosampler.

1.3 The method quantitation limit (MQL) is based on the lowest point in the initial calibration curve for a particular analyte. Detection limits (MDL, MQL, MRL...) are detailed in SOP "Determination of MDL/MQL/MRL".

1.4 Refer to Appendix A for applicable detection limits.

2.0 Summary of Method

2.1 Method 8081A is based on the solvent extraction of a sample (e.g. liquid/liquid or sonication) and subsequent concentration and clean up of the extract. The extract is then analyzed by capillary gas chromatography.

2.2 One thousand (1000) milliliters of water or 30 grams of soil is spiked with surrogate compounds and solvent extracted using Methylene Chloride for water and 1:1 Methylene Chloride-Acetone for soil samples with the appropriate preparation method (see section 7). The extract is then concentrated and exchanged to hexane using a Nitrogen blow-down technique, clean up as necessary with Florisil and analyzed by capillary GC.

2.3 LMP, Inc. utilizes simultaneous injection of the extract. The analytical systems available have dual autosamplers, dual injection ports, dual columns and dual detectors. This allows the acquisition of data from both the primary (A) and confirmation columns (B). Compound identification is based on qualitative and quantitative information from both columns.

2.4 This analytical method is based in part on methods 8000B and 8081A Solid Waste Manual SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition and the "Shell for Analytical Chemistry Requirements" USACE, EM 200-1-3. Extraction and clean-up methods are referred to in this SOP.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by the extraction and analysis of method blanks. Specific selection of reagents and solvents may be necessary.

3.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations.

3.2.1 Common flexible plastics contain varying amounts of phthalate esters, which are easily extracted or leached from such materials during laboratory operations.

3.2.2 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled

3.2.3 Avoiding contact with any plastic materials can best minimize interferences from phthalate esters.

3.3 Method interferences are reduced by proper glassware cleaning procedures. Cleaning procedures are detailed in SOP "Organic Laboratory Glassware Cleaning Procedures".

3.4 Method blanks must be extracted with each preparation batch to demonstrate that the system is free from method interferences.

3.5 High purity reagents must be used to minimize interference problems.

3.6 Contamination by carryover can occur whenever high-level and low-level samples are sequentially extracted. Extreme caution must be exercised whenever handling concentrated waste samples (e.g. product, solvent...).

4.0 Equipment and Apparatus

4.1 Gas chromatograph – Configuration 1 (This system is generally dedicated to the analysis of PCBs.)

4.1.1 Gas Chromatograph - Hewlett Packard 5890 Series II GC equipped with dual capillary column injection ports and dual electron capture detectors (ECD). The GC is equipped with a 100 place HP 7673 autosampler. Justice Innovations ChromPerfect software is utilized to acquire data where it is transferred to a central ChemServer and processed using Target3 analytical software.

4.1.2 Column 1 - 30 meter x 0.25-mm ID J&W DB-35MS 0.25 micron film thickness D&B #11123

4.1.3 Column 2 – 30 meter x 0.32-mm ID Restek RTx-CLPesticide 0.5 micron film thickness. Restek #11139

4.2 Gas chromatograph – Configuration 2 (This system is generally dedicated to the analysis of chlorinated herbicides.)

4.2.1 Gas Chromatograph - Hewlett Packard 5890 Series II GC equipped with dual capillary column injection ports and dual electron capture detectors (ECD) The GC is equipped with a 100 place HP 7673 autosampler. Justice Innovations ChromPerfect software is utilized to acquire data where it is transferred to a central ChemServer and processed using Target3 analytical software.

4.2.2 Column 1 - 30 meter x 0.32-mm ID Restek RTx-CLPesticides2 0 25 micron film thickness. Restek #11324

4.2.3 Column 2 – 30 meter x 0.32-mm ID Restek RTx-CLPesticide 0.5 micron film thickness. Restek #11139

4.3 Gas chromatograph – Configuration 3 (This system is generally dedicated to the analysis of chlorinated pesticides.)

4.3.1 Gas Chromatograph - Hewlett Packard 6890 GC equipped with dual capillary column injection ports and dual electron capture detectors (micro ECD). The GC is equipped with a 100 place HP 7683 autosampler. Justice Innovations ChromPerfect software is utilized to acquire data where it is transferred to a central ChemServer and processed using Target3 analytical software

4.3.2 Column 1 - 20 meter x 0.18-mm ID Restek RTx-CLPesticides II 0.18 micron film thickness. Restek #42302

4.3.3 Column 2 – 20 meter x 0.18-mm ID Restek RTx-CLPesticide I 0 18 micron film thickness. Restek #42102

5.0 Reagents and Standards

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Procedure (SVQAP).

5.3 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One of SW-846.

5.4 Methylene Chloride – Fisher Scientific D151-4

5.5 Hexane – Fisher Scientific H303-4

5.6 Methanol – Fisher Scientific A454-4

5.7 Stock calibration standards

5.7.1 Standards (targets and surrogates) are purchased as certified solutions from various vendors. The list of solutions, catalogue numbers and concentrations are listed in the pesticide summary table. A copy is provided in Appendix B.

5.8 Intermediate Standards. Prepare the following standards in hexane:

5.8.1 Intermediate standards (targets and surrogates) are prepared from stock standards. Refer to Appendix B **Intermediate Standards**.

5.9 Working Standards. These standards are prepared from the intermediates listed in section 5.8 and are used to perform initial calibrations. Refer to Appendix C for the initial calibration dilution schedule.

5.9.1 Prepare a "second source" initial calibration verification (ICV) standard (single and multi-component) as listed for WS #4 in Appendix C.

5.10 Matrix spike and surrogate solutions are prepared from the same standards used to prepare the initial calibration. Refer to Appendix B for spike amounts and concentrations.

5.11 The following considerations should always be followed in preparing all of the above standard solutions:

5.11.1 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Program (SVQAP).

5.11.2 Secondary dilution standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.11.3 Standards must be replaced after 6 months or sooner if comparison with the ICV standard indicates a problem

5.11.4 Stock or neat solutions and standards must be stored in proper containers, away from light and should not be transferred from the original container. The date received, expiration date and any other pertinent information should be recorded in the Reagent Reference Log. The date received must also be recorded on the standard container, clearly visible to all analysts using it

5.11.5 All intermediate and working solutions must be stored in light protected containers with Teflon lined caps at a temperature of 4oC or less.

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

6.1.1 Refer to the Quality Manual for guidance concerning containers, preservation and holding times.

6.2 Holding Times

6.2.1 Holding time for extraction is defined as the number of days from **sample collection** (e.g. sample date) to extraction.

6.2.2 Holding time for analysis is defined as the number of days from **sample extraction** in the laboratory to date injected/analyzed by the instrument.

NOTE: For volatiles (GC or GC/MS, low level or medium level) holding time is always defined as the number of days from **sample collection** until analysis.

6.3 Aqueous samples are collected in one (1) liter amber bottles with Teflon lined caps. No chemical preservation required. Soil samples are collected in 4 oz. or 8 oz. Teflon lined jars. Samples are stored at 4°C from the time of collection. All water samples must be extracted within seven (7) days of collection. Soil samples must be extracted within fourteen (14) days of collection. All extracts, soil or water must be analyzed within 40 days of extraction.

7.0 Procedure

7.1 Samples are extracted based on matrix using one of the following sample extraction methods:

Method	Matrix	Introduction
3510	Water	Separatory Funnel Liquid-Liquid Extraction
3520	Water	Continuous Liquid-Liquid Extraction
3540	Soil / Solid	Soxhlet Extraction
3550	Soil / Solid	Ultrasonic Extraction
3580	Liquid / Solid	Waste Dilution
3620	Extracts	Florisil Clean-Up

Sample preparation procedures are detailed within the above SOPs.

Batch QC requirements are discussed specifically in the Quality Manual. In general, the following batch QC samples are required for each extraction batch.

Method Blank (MB)

Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD). See section 5.10 for spiking solution information.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) – If enough sample is available.

7.2 Chromatographic conditions

7.2.1 System 1 carrier gas (Helium) flow rate: 5-10 ml/min

Temperature program

Initial temperature:	120°C hold for 1 minute
Program:	120°C to 300°C at 8.5°C/min
Final temperature:	300°C hold for 8 minutes.

7.2.2 System 2 carrier gas (Helium) flow rate: 5-10 ml/min

Temperature program

Initial temperature:	90°C, hold for 1 minute
Program:	90°C to 300°C at 11°C/min
Final temperature	300°C hold for 0 minutes.

7.2.3 System 3 carrier gas (Helium) flow rate: 0.50 ml/min

Injection port temperature:	200°C	
Detector temperature:		300°C
Purge time:		0.2 minutes
Purge flow:		15 mL/minute
Injection volume:	0.5 ul	
Temperature program		
Initial temperature:		120°C, hold for 3 minutes
Program:		120°C to 215°C at 30°C/min
		Hold for 1 minute
		215°C to 300°C at 30°C/min
Final temperature:		300°C hold for 3 minutes.
Total run time:	12.99 minutes	
Signal 1:	Range = 4	
		Attenuation = 0
Signal 2:	Range = 5	
		Attenuation = 0

7.3 Data Processing – All data for organic instruments is acquired by the networked PC/Client acquisition software (ChromPerfect, Enviroquant...). Data files are then uploaded to the NT ChemServer for processing and evaluation utilizing a networked version of the Target3 environmental data processing program. All processing methods/initial calibration are performed and maintained by the Target3 system.

7.4 Documentation

7.4.1 Daily Run Log. The samples analyzed for each analytical sequence are recorded on the daily run log. This log is identified by the analytical system and date analyzed and is used to record the analytical sequence prior to entry in the data acquisition system. A copy of the log(s) is included in the sequence package Refer to Appendix F

7.4.2 Sequence CheckList. This list is specific for this analytical method and is designed to ensure that all major QC elements of an analytical sequence are accounted for and evaluated. In addition, QC requirements for the preparation batch are also addressed. Refer to Appendix F.

7.5 Daily Instrument Maintenance. Due to the sensitivity of electron capture detectors (ECD), regularly scheduled maintenance is required to enable the analyst to obtain usable data as needed from the system Maintenance should be performed daily, prior to the analysis of standards and samples.

7.5.1 Daily maintenance consists of:

- ❑ Replace septa. Allow a maximum of 50 injections.
- ❑ Replace injection port seal and inlet sleeve.
- ❑ Cut approximate 1 to 2 inches from the head of the capillary column.
- ❑ Rinse the lumen of the inlet nut with hexane and blown dry with a micro-duster to remove any septum particles.
- ❑ Bake-out the GC at 310°C between sequences.

7.6 Retention Time Windows (RTW). The process of defining RTWs is detailed in the Quality Manual. By definition, this SOP requires that the default standard deviation of 0.0033 minutes (window = 0.01 minutes) be used. RTW reports are generated periodically to monitor the analytical systems and ensure that the default value remains appropriate.

Note: The center of the absolute retention time window for each analyte is its retention time in the mid-concentration standard analyzed during the initial calibration.

7.7 Injection Port Inertness Check. Prior to the analysis of any standards or samples, the inertness of the GC system must be demonstrated for each analytical sequence:

7.7.1 DDT and Endrin are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated with high boiling residue from sample injection.

7.7.2 Check for degradation problems by injecting a standard containing only 4, 4'-DDT and Endrin. Presence of 4, 4'-DDE, 4, 4'-DDD, Endrin ketone or Endrin aldehyde indicates breakdown.

7.7.3 If degradation of either DDT or Endrin exceeds 15%, take corrective action as specified in section 7.5 before proceeding with any analysis.

7.7.4 The stock solution used for breakdown evaluation is purchased from either Ultra Scientific (ISM-450) or Accustandard (M8081-D5) and diluted to a concentration of 0.04/0 08 ug/mL Endrin and DDT.

$$\% \text{ breakdown of DDT} \quad \frac{\text{sum of degradation peak areas (DDD + DDE)}}{\text{sum of all peak areas (DDT + DDE + DDD)}} \times 100$$

$$\% \text{ breakdown of Endrin} \quad \frac{\text{sum of degradation peak areas (aldehyde + ketone)}}{\text{sum of all peak areas (Endrin + aldehyde + ketone)}} \times 100$$

7.8 Initial Calibration - The external standard procedure is used to calibrate the chromatographic system. Prepare the calibration standards using the procedures outlined in section 5. Calibration procedures are detailed in the Quality Manual

7.8.1 Single Component Pesticides. Calibrate the GC with an initial eight- (8) point calibration using working standards as in Section 5.9. The lowest calibration standard (WS-1) is below the method quantitation limit (MQL) of 0.04 ug/L for water and 2.0 ug/Kg for soil. The highest calibration standard (WS-8) defines the upper linear range of the chromatographic system.

7.8.2 Multi-Component Pesticides A single mid-range standard is analyzed for Chlordane and Toxaphene to aid in pattern recognition. If a multi-component pesticide is identified in a sample, the system is re-calibrated for that pesticide with a minimum of three (3) standards. The extract is re-analyzed with the new calibration and quantitated. Calibrations for the multi-component pesticides are based on three (3) to five (5) major characteristic peaks.

7.8.3 Note: When evaluating the initial calibration using Target 3 software, a minimum of five calibration levels must be used. Standard WS-2 is required for this method and must not be disabled. If the use of WS-2 does not meet initial calibration criteria, corrective action must be taken to allow the system to be calibrated with WS-2.

7.8.4 Each calibration standard is directly injected via autosampler. This technique will be used for all subsequent injections made on the chromatographic system. The calibration factor (CF) is automatically calculated by the Target3 system.

$$CF \quad \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

Average CF Calibration. This is the first and best option that the analyst should consider and use whenever possible. To validate the initial calibration for this option, the percent relative standard deviation (RSD) of the CFs must be less than or equal to 20%.

$$\text{mean CF} \quad \overline{CF} \quad \frac{\sum_{i=1}^{n} CF}{n}$$

Linear Regression. If the %RSD of the average CF option is greater than 20% or at the discretion of the analyst, a linear regression calibration may be used. The y-intercept must not be above the lowest calibration point in order to use this option. In order to be used for quantitative purposes, r^2 must be greater than or equal to 0.990

$$SD \quad \sqrt{\frac{\sum_{i=1}^{n} (CF - \overline{CF})^2}{n-1}} \qquad RSD \quad \frac{SD}{\overline{CF}} \times 100$$

7.8.4.1 Quadratic. Due to the nature and sensitivity of the ECD, this option is allowed specifically for the analysis of chlorinated pesticides. This option may be used at the discretion of the analyst. The y-intercept must not be above the lowest calibration point in order to use this option. In order to be used for quantitative purposes, r^2 must be greater than or equal to 0.995.

7.8.4.2 The analyst should not force the line through the origin, but have the intercept calculated from the data points. In addition, do not include the origin (0, 0) as a calibration point. A visual inspection of the calibration curve should also be used as a diagnostic tool when nonlinear behavior is observed to verify if there is a large percentage error in any particular portion of the calibration curve.

7.8.5 If the initial calibration curve does not meet the above criteria, a problem exists. Identify and correct the problem. Perform the initial calibration again. Sample analysis may not begin until the initial calibration has been validated.

7.9 Initial Calibration Verification (ICV). The initial calibration is verified as accurate by the analysis of an independent calibration verification standard. This standard is prepared independently of the ICAL from a second source. The ICV standard must meet method continuing calibration verification (CCV) criteria in order to validate the initial calibration.

7.10 As a rule, an initial calibration is performed for each analytical sequence. The ICV is analyzed after the last calibration standard.

7.11 Continuing Calibration Verification (CCV). The current initial calibration (CF and retention time) must be verified within each analytical sequence every 20 samples and at the end of the sequence. Verification is accomplished by the analysis of the mid-range standard WS-4. CCVs are analyzed in pairs (e.g. CV1A, CV1B).

Calculate the % difference where CFv is the calibration factor from the analysis of the verification standard, and CF is the mean calibration factor from the initial calibration.

$$\% \text{ Difference} = \frac{CF_v - \overline{CF}}{\overline{CF}} \times 100$$

7.11.1.1 The % difference for the calibration verification standard should not exceed ±15% for each analyte.

7.11.1.2 SW-846 also allows for the use of the averaged % difference of **all calibrated analytes.** The average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project. For Level III and IV data packages, CCV reports are provided along with a case narrative. The average % difference for the calibration verification standard must not exceed ±15. The maximum allowable % difference for any individual analyte must not exceed 30

7.11.1.3 SW-846 specifies that samples analyzed using external standards must be bracketed by periodic analyses of standards that meet the QC acceptance criteria (e.g., calibration and retention time). The results from these bracketing standards must meet the calibration verification criteria and the retention time criteria as listed above. However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >15%, and the analyte was not detected in any of the previous samples during the analytical shift, then the sample extracts do not need to be reanalyzed. The verification standard has demonstrated that the analyte would have been detected were it present.

7.11.2 All target analytes and surrogates should fall within previously established retention time windows.

7.11.3 If the CV does not meet the above criteria:

7.11.3.1 Evaluate the second CV for the failing analytes. If the second CV passes for those analytes, the sequence is valid.

7.11.3.2 If the second CV fails for the analytes, then samples analyzed before and after the failing CV may need re-analysis.

7.12 Gas chromatographic analysis

7.12.1 All extracts (standards and samples) are introduced into the gas chromatograph using automated direct injection. Samples are analyzed in a set referred to as an analytical sequence.

7.12.1.1 Sequences are initiated on the ChromPerfect data system. The information entered into the sequence file will be uploaded with the data file to the Target server. Sequences procedures are detailed in the pesticide summary table.

7.12.1.2 The sequence is identified by the system identifier and the date of the analyses:

P3030901	
P3	= Pesticide System 3
030900	= Date of Analysis (03/09/00)
01	= First sequence of the day

7 12.1.3 Data files are defined by the sequence id plus the data file number:

P3030901.01R – 1st data file for this sequence.
P3030901.02R – 2cnd data file for this sequence.

7 12.1.4 A pesticide evaluation mix (PEM) is then analyzed to monitor breakdown (section 7 7 3).

7.12.1.5 Typically an initial calibration followed by samples interspersed with mid-range calibration verification (CV) standards are analyzed. The sequence ends when the set of samples has been injected or when QC criteria has been exceeded (%D >15) The analytical sequence may begin with a continuing calibration verification followed by samples if the 15% criteria is met for all target analytes of interest. A calibration verification standard must be analyzed after each group of 20 samples and at the end of the analytical sequence.

7.12.1.6 Detailed information concerning the analytical sequence is provided in the pesticide summary table.

7.12.2 A sequence checklist must be completed for each analytical sequence. This checklist summarizes the method requirements and allows the analyst to record information specific to the analytical sequence.

7.12.3 Extracts (sample and lab QC) are prepared in duplicate to allow the dual injection on both the primary and confirmation column.

7.12.3.1 100ul glass inserts are inserted in the autosampler vials. If dilutions are to be performed, no insert is used

7.12.3.2 A portion of the sample extract is transferred to two (2) vials that are identically labeled. One will be placed in the autosampler for injection of the front column while the second will be placed to be injected on the back column.

7.12.4 Tentative identification of a single component analyte occurs when a peak from a sample extract falls within the absolute retention time window Confirmation occurs when this analyte falls within the absolute retention time window for the second column. Target Form 10, Pesticide Dual Column Confirmation Check, is used to summarize the identified analytes (Appendix F).

7.12.4 1 Data for the primary analysis is reviewed initially for the tentative identification of an analyte.

7.12.4.2 If an analyte is identified in the primary, the confirmation analysis is reviewed for that analyte.

7.12.4.3 Use the Target Form 10 to perform an evaluation as to whether an analyte is confirmed. Calculations are discussed in Section 7.13. The relative percent difference of the primary and confirmation results should be less than 40% for the analyte to be reported. The analyst should also evaluate the RPD of the surrogate compounds to monitor the validity of the 40% RPD.

7.12.4.4 GC/MS confirmation may be used in circumstances where the concentration is high enough.

7.12.5 Identification of multi-component analytes (e.g. Chlordane and Toxaphene) is based on the characteristic fingerprint retention time and shape of the indicator peaks. Three (3) to five (5) major peaks are selected for use in qualitative and quantitative identification.

7.12.5.1 Data for the primary analysis is reviewed initially for the tentative identification of the analyte.

7.12.5.2 If an analyte is identified in the primary, the confirmation analysis is reviewed for that analyte.

7.12.5.3 Use the Target Form 10t o perform an evaluation as to whether an analyte is confirmed. Calculations are discussed in section 7.13. The relative percent difference of the primary and confirmation results should be less than 40% for the analyte to be reported. The analyst should also evaluate the RPD of the surrogate compounds to monitor the validity of the 40% RPD.

7.12.5.4 GC/MS confirmation may be used in circumstances where the concentration is high enough.

7.13 Calculations. All calculations are handled by the Target3 environmental sample processing software Quantitation reports are generated for all samples (e.g. sample, blanks, controls…). These reports summarize the analytes identified, retention, area/height, on-column amount and final concentration adjusted for dilution and/or sample size.

7.13.1 Quantitation of single component analytes are determined by comparing the response in the sample to the CF from the initial calibration. Based on review of the initial calibration and calibration verifications, one column is assigned as primary and one is assigned as confirmation for the analytical sequence.

7.13.2 Quantitation of Toxaphene and Chlordane is accomplished according to the following:

7.13.2.1 Upon identification of a multi-component analyte, the sample must be re-analyzed after a minimum three (3)-point initial calibration (Toxaphene or Chlordane).

7.13.2.2 Quantitation is performed by comparing the response in the sample of 4 to 6 characteristic peaks for Toxaphene or 3 to 5 characteristic peaks for Chlordane the CF from the initial calibration of the **same characteristic peaks**

7.13.2.3 Based on review of the initial calibration and calibration verifications, one column is assigned as primary and one is assigned as confirmation for the analytical sequence.

7.13.3 If the response of any confirmed analyte exceeds the upper calibration standard, the sample must be diluted and reanalyzed. It is recommended that samples be diluted so that all peaks are on scale and have not exceeded the linear range of the detector. If peaks are off scale, the judgment of the analyst is critical in determining if further dilutions are needed

7.13.4 Water Samples

where:

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

A = Area (or height) of the peak for the analyte in the sample.
Vt = Total volume of the concentrated extract (ml) - default 10.
D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.
CF = Mean calibration factor from the initial calibration
Vi = Volume of the extract injected (µL) – default 1.
Vs = Volume of the aqueous sample extracted (ml) - default 1000.

Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

7 13.5 Solid Samples

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(V_t)(D)}{(\overline{CF})(V)(W_s)}$$

All values same as for water except:
Ws = Weight of sample extracted or purged (g). Either the wet weight or dry weight. Unless otherwise specified, all soil results are reported on a dry weight basis. Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

7.13.6 When sample results are confirmed (single or multi-component) the agreement between the quantitative results should be evaluated after the identification has been confirmed (e.g. Form 10). The relative percent difference (RPD) defines the difference between the two (2) results It should be noted that RPDs are calculated when at least one results (from the primary or confirmation column) is greater than the quantitation limit.

7.13.6.1 Results are reported, when possible, from the column assigned as primary

7.13.6.2 If one result is significantly higher (e g. >40%), check the chromatogram for any obvious signs of matrix interference such as overlapping peaks. If interference is obvious, the result should be reported from the second column

7.13.6.3 If no anomalies are noted, then whenever possible, the high result should be reported. However, this may be precluded by the assignment of the column as confirmation.

7.14 Instrument Maintenance.

7.14 1 Routine maintenance is an integral part of maintaining a productive quality analytical system throughout the laboratory. Instruments must be maintained at optimum performance to ensure the highest level of quality and sample throughput.

7 14.2 In addition, documentation of the maintenance in the instrument maintenance logbook will allow the analyst and supervisor to track the performance of the instrument, identify trends and minimize overall downtime.

7.14.2.1 Daily maintenance is described in section 7.5.

8.0 Quality Control/Quality Assurance/Corrective Action

8.1 Refer to the Laboratory Quality Management Plan (LQMP) for QC procedures and evaluations to be employed for this method.

8.2 A summary of control limits and spike concentrations can be provided to support this SOP.

8.3 Corrective Actions are those actions performed to correct situations that are deemed adverse to data quality. Corrective actions are addressed in section 10 of the LQMP and in the SOP "Non-conformance and Corrective Action." Corrective actions are usually addressed within the procedure section of the analytical SOP. Examples of situations requiring corrective action:

8.3.1 Initial calibration does not meet criteria.

8.3.1.1 Review the initial calibration to see if any one (1) point appears as a significant outlier. This standard(s) may be re-analyzed and replaced in the initial calibration.

8.3.1.2 Compare calibration responses to previous calibrations to identify significant differences.

8.3.1.3 Review the calibration procedure and standards to ensure that they were prepared properly.

8.3.1.4 Evaluate the system and perform maintenance as necessary.

8.3.1.5 Perform the initial calibration again.

8.3.2 Calibration verification does not meet criteria.

8.3.2.1 Re-analyze the verification for the failing analytes. If these pass, the analytical sequence may continue. If the re-analysis fails for those analytes, the analytical sequence must be stopped and the system evaluated.

8.3.2.2 The use of the average percent difference for all calibrated analytes may be employed by the analyst based on discussion with the section supervisor and project manager.

8.3.3 Sample result above the high point in the initial calibration.

8.3.3.1 If the result is within 10% of the high point, the result is considered valid, flagged as "E – Exceeds calibration range" and reported. This result should be discussed in a Case Narrative.

8.3.3.2 If the result not within 10% of the high point, the result may be reported with approval from the project manager This approval must take into account the data quality objectives of the project.

8.3.3.3 Re-analyze the sample at an appropriate dilution.

9.0 Data Validation

9.1 Refer to the Quality Manual for data validation procedures and guidelines.

10.0 Training & Training Validation

10.1 Refer to the Laboratory Employee Training SOP for training procedures and guidelines.

11.0 Waste Management and Disposal

11.1 Refer to the Waste Management Plan for waste disposal procedures.

12.0 Health and Safety

12.1 Refer to the Chemical Hygiene and Laboratory Safety Plan for health and safety procedures and guidelines.

13.0 References

13.1 Solid Waste Manual, SW846 Update III, December 1996.

13.2 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements EM 200-1-3.

13.3 Standard Methods for the Examination of Water and Wastewater, 18th and 20th Edition.

13.4 EPA, Methods for Chemical Analysis of Water and Wastes, EPA –600/4-79-020, March 1983.

13.5 NELAC, Quality Systems, Revision 14, June 29, 2000.

13.6 NELAC, Program Policy and Structure, Revision 13, June 29, 2000.

13.7 40 CFR Part 136 Appendix A.

13.8 EPA Guidance for Preparing Standard Operating Procedures (SOPs), EPA QA/G-6, EPA/240/B-01/004, March 2001

13.9 EPA 2185 – Good Automated Laboratory Practices

13.10 OSHA Laboratory Standard, 29 CFR 1910.1450.

13.11 OSHA Compliance Guide, Kirk H Ray, 8th Edition.

13.12 *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.

13.13 Laboratory Safety in Practice. A Comprehensive Compliance Program and Safety Manual.

13.14 *"Safety in Academic Chemistry Laboratories"*, American Chemical Society Publication, Committee on Chemical Safety .

13.15 *"Carcinogens – Working with Carcinogens"*, Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

Appendix A
Detection Limits

Method Quantitation Limits			
		ug/L	ug/Kg
ANALYTE:	**CAS #**	**Water**	**Soil**
Single-Component Pesticides			
alpha-BHC	319-84-6	0.04	2.0
beta-BHC	319-85-7	0.04	2.0
delta-BHC	319-86-8	0.04	2.0
gamma-BHC (Lindane)	58-89-9	0 04	2.0
Alpha-chlordane	5103-71-9	0.04	2.0
Gamma-chlordane	5103-74-2	0.04	2.0
Chlorpyrifos	2921-88-2	0.04	2.0
Heptachlor	76-44-8	0.04	2.0
Heptachlor Epoxide	1024-57-3	0.04	2.0
Aldrin	309-00-2	0.04	2.0
Dieldrin	60-57-1	0.04	2.0
Endrin	72-20-8	0.04	2.0
Endrin Aldehyde	7421-93-4	0.04	2.0
Endrin Ketone	53494-70-5	0.04	2 0
p,p'-DDE	72-55-9	0.04	2.0
p,p'-DDD	72-54-8	0.04	2.0
p,p'-DDT	50-29-3	0.04	2.0
Endosulfan I	959-98-8	0.04	2.0
Endosulfan II	33213-65-9	0 04	2.0
Endosulfan sulfate	1031-07-8	0.04	2.0
Methoxychlor	72-43-5	0.04	2.0
Multi-Component Pesticides			
Chlordane	57-74-9	0 25	20
Toxaphene	8001-35-2	2.5	200
Surrogates			
Tetrachloro-m-xylene (TMX)	877-09-8	31- 96	39-130
Decachlorobiphenyl (DCB)	2051-24-3	34-115	64-154

Nominal Sample Size for Water: **1000mls**
Nominal Sample Size for Soil: **30g**
Nominal Final Volume: **10mls**

Appendix B

Standard Solutions

Stock Solution	Description	Use	Conc ug/ml	Solvent	Vendor
ISM-450	Pest Evaluation Mix (PEM)	PEM	1 / 2	Isooctane	Ultra
PPM-808C	Pesticides - Targets	ICAL	1,000	Hex/Toluene	Ultra
P-017S-H-10X	Chlordane - Target	ICAL/MS	1,000	Hexane	Accustandard
P-093S-H-50X	Toxaphene - Target	ICAL/MS	5,000	Hexane	Accustandard
ISM-320	DCB/TMX - Surrogates	ICAL/Samp/MS	200	Acetone	Ultra
P-0942-10X	Dursban	ICAL/Samp/MS	1,000	Hexane	Accustandard
ACE-8081-SC	Pesticides - Target	ICV	1,000	Hex/Tol	Accustandard
4-8065	Chlordane - Target	ICV	1,000	Isooctane	Supelco
S-3535	Toxaphene - Target	ICV	1,000	Hexane	Protocol
CLP-032R	DCB/TMX - Surrogates	ICV	200	Acetone	Accustandard
US-127-4	Pesticides - Targets	LCS/MS	2,000	Hex/Tol	Ultra

Intermediates		Initial Volume(uls)	Final Volume(mls)	Solvent	Final Conc(ug/ml)
ICAL	PPM-808C - Targets	200	10	Hexane	20 0
	P-0942-10X - Dursban	200	10	Hexane	20 0
	ISM-320 - Surrogates	1000	10	Hexane	20 0
	P-017S-H-10X - Chlordane	1000	10	Hexane	100
	ISM-320 - Surrogates	1000	10	Hexane	20 0
	Toxaphene	No Intermediate			
	ISM-320 - Surrogates	1000	10	Hexane	20 0
Surrogate	ISM-320 - Surrogates	200	100	Acetone	0 40
LCS/MS	US-127-4 - Targets	50	100	Acetone	1 00
	P-0942-10X	100	100	Acetone	1 00

QC		FC ug/ml	FV ug/ml	FC 250mls ug/L	FC 1000mls ug/L	FC 30g ug/Kg
Surrogate - Int	ISM-320					
	Spike 1ml per 250/1000mls or 30g Final Volume = 10mls					
	TMX/DCB	0 40	0 04	1.6	0 40	13 3

Appendix C

Initial Calibration Dilution Schedules

Standards Used: Intermediates		PPM-808C - Single Component Targets				P-017S-H-10X Chlordane			
		P-0942-10X - Dursban				P-093S-H-10X Toxaphene			
		ISM-320 - Surrogates							
Current - Ultra									
	Final Volume 100mls of Hexane								
Analyte PPM-808C	**Nominal**	**WS-1**	**WS-2**	**WS-3**	**WS-4**	**WS-5**	**WS-6**	**WS-7**	**WS-8**
ISM-320	**ug/ml**	**2**	**20**	**50**	**100**	**150**	**200**	**300**	**2000**
Aldrin	20	0.0004	0 004	0.010	0 020	0 030	0 040	0.060	0.400
alpha-BHC	20	0 0004	0.004	0 010	0.020	0 030	0.040	0 060	0.400
beta-BHC	20	0 0004	0 004	0 010	0 020	0 030	0 040	0 060	0 400
delta-BHC	20	0.0004	0 004	0 010	0.020	0.030	0.040	0.060	0.400
gamma-BHC	20	0 0004	0 004	0.010	0 020	0.030	0 040	0 060	0 400
alpha- Chlordane	20	0.0004	0 004	0 010	0 020	0.030	0 040	0 060	0 400
gamma-Chlordane	20	0.0004	0.004	0.010	0.020	0.030	0.040	0 060	0 400
4,4-DDD	20	0 0004	0 004	0 010	0 020	0 030	0 040	0 060	0.400
4,4-DDE	20	0 0004	0.004	0 010	0.020	0.030	0 040	0 060	0 400
4,4-DDT	20	0.0004	0 004	0 010	0 020	0 030	0 040	0 060	0 400
Dieldrin	20	0.0004	0.004	0 010	0 020	0 030	0.040	0 060	0.400
Endosulfan I	20	0.0004	0.004	0 010	0 020	0.030	0 040	0.060	0.400
Endosulfan II	20	0 0004	0 004	0 010	0 020	0.030	0 040	0 060	0 400
Endosulfan Sulfate	20	0.0004	0 004	0 010	0 020	0 030	0 040	0 060	0 400
Endrin	20	0 0004	0.004	0.010	0.020	0.030	0 040	0.060	0.400
Endrin Aldehyde	20	0.0004	0.004	0 010	0.020	0 030	0.040	0.060	0.400
Endrin Ketone	20	0.0004	0 004	0 010	0 020	0 030	0 040	0 060	0 400
Heptachlor	20	0.0004	0.004	0.010	0.020	0 030	0 040	0.060	0.400
Heptachlor Epoxide(b)	20	0 0004	0.004	0 010	0 020	0 030	0 040	0.060	0 400
Methoxychlor	20	0 0004	0 004	0 010	0.020	0.030	0.040	0 060	0 400
TMX - Surrogate	20	0 0004	0 004	0 010	0 020	0 030	0 040	0 060	0.400
DBC - Surrogate	20	0.0004	0 004	0 010	0 020	0 030	0 040	0.060	0.400
FV = 100ml Hexane		**WS-1**	**WS-2**	**WS-3**	**WS-4 (ICV)**	**WS-5**	**WS-6**		
Targets/Surrogates	ug/ml ul	25	50	200	500	1000	2000		
Chlordane P-017S-H-10X	100	0 025	0 050	0 200	0 500	1 000	2 000		
TMX - Surrogate	20	0 005	0 010	0.040	0.100	0.200	0 400		
DBC - Surrogate	20	0.005	0 010	0 040	0 100	0 200	0 400		

		WS-1	WS-2	WS-3	WS-4 (ICV)	WS-5			
FV = 50ml Hexane	ug/ml ul	2.5	5	10	20	40			
Toxaphene P-093S-H-10X	5000	0.250	0.500	1 000	2 000	4 000			
TMX - Surrogate*	20	0 010	0 002	0.004	0 008	0 016			
DBC - Surrogate*	20	0 010	0 020	0.080	0 200	0 400			
	*	25	50	200	500	1000			

Appendix E

Spiking Solutions

QC		FC ug/ml	FV ug/ml	FC 250 mls ug/L	FC 1000mls ug/L	FC 30 g ug/Kg
Surrogate- Int	ISM320 Spike 1 ml per 250/1000 mls or 30g Final Volume = 10 mls					
	TMC/DCB	0 40	0.04	1.6	0.40	13.3
LCS/ICV6	US127-4/P0942-10X Spike 1 ml per 250/1000 mls or 30g Final Volume = 10mls					
	Targets	1.00	0.10	4.00	1.00	33.3

Appendix F

Run Log

Sequence Check List – Single Component Analytes
Sequence Check List – Multi-Component Analytes

Pesticide Dual Column Confirmation Check

8772024

Standard Operating Procedure For The Determination of Chlorinated Herbicides by Method 8151A

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

1.1 This method is used to determine the concentration of various chlorinated herbicides. This SOP addresses the requirements of SW-846 methods 8000B (Revision 2 December 1996) and 8151A (Revision 1 December 1996). This method is applicable to the analysis of water, soil, liquid and solid samples.

1.2 Instrumentation: Dual capillary GC equipped with dual electron capture detectors (ECD) and autosampler.

1.3 The method quantitation limit (MQL) is based on the lowest point in the initial calibration curve for a particular analyte. Detection limits (MDL, MQL, MRL...) are detailed in SOP "Determination of MDL/MQL/MRL".

1.4 Refer to Appendix A for applicable detection limits.

2.0 Summary of Method

2.1 Method 8151A is based on the solvent extraction of a sample (e.g. liquid/liquid or sonication) and subsequent concentration and derivatization of the extract. The extract is then analyzed by capillary gas chromatography.

2.2 One thousand (1000) milliliters of water or 30 grams of soil is spiked with surrogate compounds. Diethyl ether extraction solvent is used for aqueous samples and methylene chloride is used for soil samples. The extract is then esterified with diazomethane. The derivatives are determined by GC/ECD.

2.3 LMP, Inc utilizes simultaneous injection of the extract. The analytical systems available have dual autosamplers, dual injection ports, dual columns and dual detectors. This allows the acquisition of data from both the primary (A) and confirmation columns (B). Compound identification is based on qualitative and quantitative information from both columns.

2.4 This analytical method is based in part on methods 8000B and 8151A Solid Waste Manual SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition and the "Shell for Analytical Chemistry Requirements" USACE version 1 0 2 Nov 98. Extraction methods are detailed in this SOP.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by the extraction and analysis of method blanks Specific selection of reagents and solvents may be necessary.

3.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in herbicide determinations.

3.2.1 Common flexible plastics contain varying amounts of phthalate esters, which are easily extracted or leached from such materials during laboratory operations.

3.2.2 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

3.2.3 Avoiding contact with any plastic materials can best minimize interferences from phthalate esters.

3.3 Method interferences are reduced by proper glassware cleaning procedures. Cleaning procedures are detailed in SOP "Organic Laboratory Glassware Cleaning Procedures".

3.4 Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure.

3.5 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water. Sodium sulfate must be acidified.

3.5.1 Sodium sulfate, if over acidified through improper preparation, can cause the structural degradation of the chlorinated herbicides to be analyzed. Care must be taken to ensure that sodium sulfate is properly acidified.

3.5.2 Refer to Section 5 for instructions on how to prepare an acidic solution to rinse all glassware before using.

3.6 Method blanks must be extracted with each preparation batch to demonstrate that the system is free from method interferences.

3.7 High purity reagents must be used to minimize interference problems.

3.8 Contamination by carryover can occur whenever high-level and low-level samples are sequentially extracted. Extreme caution must be exercised whenever handling concentrated waste samples (e.g product, solvent, etc.).

3.9 Sample extracts should be dry (free of water contamination) prior to methylation or poor recoveries may result.

4.0 Equipment and Apparatus

4 1 Gas chromatograph – Configuration 2 (This system is generally dedicated to the analysis of chlorinated herbicides)

4.1.1 Gas Chromatograph - Hewlett Packard 5890 Series II GC equipped with dual capillary column injection ports and dual electron capture detectors (ECD). The GC is equipped with a 100-place HP 7673 autosampler. Justice Innovations ChromPerfect software is utilized to acquire data where it is transferred to a central ChemServer and processed using Target3 analytical software.

4.1.2 Column 1 - 30 meter x 0.32-mm ID Restek RTx-CLPesticides2 0.25 micron film thickness Restek #11324

4.1 3 Column 2 – 30 meter x 0.32-mm ID Restek RTx-CLPesticide 0 5 micron film thickness. Restek #11139

4.2 Ultrasonic Extraction System. Tekmar dual horn unit with ¾" horns and sonabox enclosure.

4.3 Solvent Evaporation/Concentration Apparatus. Labconco Rapid N_2 Evaporation System

4.4 Alternate Solvent Concentration Apparatus - Kuderna-Danish (K-D). (If Labconco systems are unavailable)

4.4.1 Concentrator tube - 10-mL graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.4.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4 4.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.5 Diazomethane Generator – Assemble from two 20 mm x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Appendix F.

4.6 Glassware

4.6.1 Beaker – 250ml

4.6.2 Separatory funnel – 2 liter with PTFE stopcock

4.6.3 Centrifuge bottle – 500ml Pyrex® 1260 of equivalent

4.6.4 Erlenmeyer Flasks – 500ml

4.6.5 Pipet – 1ml calibrated serological

4.6.6 Vials – 40ml with Teflon septa.

5.0 Reagents and Standards

5.1 Reagent grade chemicals shall be used in all tests Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Procedure (SVQAP).

5.3 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One of SW-846.

5.4 Diethyl Ether, Fisher Scientific E199-4

5.5 Methylene Chloride. Fisher Scientific D151-4

5.6 Hexane. Fisher Scientific H303-4

5.7 Methanol. Fisher Scientific A454-4

5.8 Isooctane. Fisher Scientific

5.9 Esterification Reagents

5.9.1 Carbitol (diethylene glycol monoethyl ether). Optional, for producing alcohol-free diazomethane.

5.9.2 N-methyl-N-nitroso-p-Toluenesulfonamide (Diazald)

5.9.3 Silicic Acid (H_2SiO_5). 100-mesh powder stored at 130°C

5.9.4 37 % KOH Solution (w/v): Dissolve 37 grams of potassium hydroxide pellets in to 100 mL of deionized water.

5.10 Sodium sulfate (granular, acidified, anhydrous Na_2SO_4). Purify by heating at 400 °C for 4 hours in a shallow tray, or by cleaning the sodium sulfate with methylene chloride. Acidify by slurring 100-g sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 ml of concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of organic-free reagent water and measure the pH of the mixture. It must be below a pH of 4 Store the remaining solid at 130oC.

5.11 pH Adjustment Solutions

5.11.1 Sodium Hydroxide (NaOH). 6N – 240grams of NaOH to 1000ml or organic free water.

5.11.2 Sulfuric Acid (H_2SO_4). 12N – Add 334mls of concentrated sulfuric acid very slowly to 1 liter of organic free water. **REMEMBER, ALWAYS ADD ACID TO WATER!!!** This translates to 0.3mls of sulfuric acid per ml of organic free water. Assign a SRN and store in a labeled glass container.

5.12 Glassware Rinsing Solution. Add 1.0ml of concentrated sulfuric acid to 1000mls of organic free water.

5.13 Stock calibration standards

5.13.1 Standards (targets and surrogates) are purchased as certified solutions from various vendors. The list of solutions, catalogue numbers and concentrations are listed in the herbicide summary table. A copy is provided in Appendix B.

5.14 Intermediate Standards. Prepare the following standards in hexane:

5.14.1 Intermediate standards (targets and surrogates) are prepared from stock standards. Refer to Appendix B **Intermediate Standards**.

5 15 Working Standards These standards are prepared from the intermediates listed in section 5.8 and are used to perform initial calibrations. Refer to Appendix C for the initial calibration dilution schedule

5.15 1 Prepare a "second source" initial calibration verification (ICV) standard (single and multi-component) as listed for WS#4 in Appendix C.

5.16 Matrix spike and surrogate solutions are prepared from the same standards used to prepare the initial calibration. Refer to Appendix B for spike amounts and concentrations. QC limits are provided in Appendix D

5.17 The following considerations should always be followed in preparing all of the above standard solutions

5.17.1 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Program (SVQAP).

5 17.2 Secondary dilution standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.17.3 Standards must be replaced after 6 months or sooner if comparison with the ICV standard indicates a problem.

5.17 4 Stock or neat solutions and standards must be stored in proper containers, away from light and should not be transferred from the original container The date received, expiration date and any other pertinent information should be recorded in the Reagent Reference Log. The date received must also be recorded on the standard container, clearly visible to all analysts using it.

5.17.5 All intermediate and working solutions must be stored in light protected containers with Teflon lined caps at a temperature of 4oC or less.

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

6.1.1 Refer to the Quality Manual for guidance concerning containers, preservation and holding times.

6.2 Holding Times

6.2.1 Holding time for extraction is defined as the number of days from ***sample collection*** (e.g. sample date) to extraction.

6.2.2 Holding time for analysis is defined as the number of days from ***sample extraction*** in the laboratory to date injected/analyzed by the instrument.

NOTE: For volatiles (GC or GC/MS, low level or medium level) holding time is always defined as the number of days from ***sample collection*** until analysis.

6.3 Aqueous samples are collected in one (1) liter amber bottles with Teflon lined caps. No chemical preservation required. Soil samples are collected in 4 oz. or 8 oz. Teflon lined jars. Samples are stored at 4°C from the time of collection. All water samples must be extracted within seven (7) days of collection. Soil samples must be extracted within fourteen (14) days of collection. All extracts, soil or water must be analyzed within 40 days of extraction.

Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), Method 8151 describes a hydrolysis step that can be used to convert herbicide esters into the acid form prior to analysis. Herbicide esters generally have a half-life of less than one week in soil.

7.0 Procedure

7.1 Samples are extracted based on matrix using one of the following sample extraction methods:

Matrix	Introduction
Water	Separatory Funnel Liquid-Liquid Extraction
Soil / Solid	Ultrasonic Extraction
Liquid / Solid	Waste Dilution

Sample preparation procedures are detailed within this SOP.

Batch QC requirements are discussed specifically in the Quality Manual. In general, the following batch QC samples are required for each extraction batch:

Method Blank (MB)

Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD). See section 5.10 for spiking solution information.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) – If enough sample is available.

7.2 Extraction Procedure for Waters

7.2.1 Using a graduated cylinder, transfer a 1-L sample aliquot to a 2-L separatory funnel. Spike the sample with the appropriate surrogate solution (section 5)

7.2.2 Add 250 g of NaCl to the sample, seal, and shake to dissolve the salt.

7.2.3 Use the following procedure only of herbicide esters, in addition to herbicide acids, are to be determined.

7.2.3.1 Add 17 mL of 6N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper. If the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6N NaOH. Let the sample sit at room temperature until the hydrolysis step is completed (usually 1-2 hours), shaking the separatory funnel and contents periodically.

7.2.3.2 Add 60 mL of methylene chloride to the sample bottle and rinse both the bottle and the graduated cylinder. Transfer the methylene chloride to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes If the emulsion interface between the layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the separation phase. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase.

7.2.3.3 Add a second 60-ml volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, discarding the methylene chloride layer. Perform a third extraction in the same manner.

7.2 4 Add 17 mL of cold (4°C) 12 N sulfuric acid to the sample, seal, and shake to mix. Check the pH of the sample with pH paper. If the sample does not have a pH less than or equal to 2, adjust the pH by adding more acid.

7.2.5 Add 120 mL diethyl ether to the sample, seal, and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. Filter the ether using a funnel with Whatman 41 filter paper containing acidified sodium sulfate.

7.2.6 Add 60 mL of diethyl ether to the sample, and repeat the extraction procedure a second time, combining the extracts in the 500-mL Erlenmeyer flask. Perform a third extraction with 60-mL diethyl ether in the same manner. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

NOTE: The drying step is very critical to ensuring complete esterification Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add
a few additional grams of acidified sodium sulfate and again test by swirling.

The 2-hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

7.2.7 Quantitatively transfer the dried extract through a funnel with a Whatman 41 filter paper and collect in the nitrogen-evaporating flask.

7.2.8 Evaporate the extract on using the Nitrogen evaporator to a volume of approximately 1-mL.

7.2.9 Dilute the extract with 1 mL of isooctane and 0 5 mL of methanol. Dilute to a final volume of 4 mL with diethyl ether The sample is now ready for methylation with diazomethane.

7.2.10 Proceed to the esterification step.

7.3 Extraction Procedure for Soils

7.3.1 Add 30 g (dry weight) of the well-mixed solid sample to a 250-mL beaker. Adjust the pH to 2 with 2 drops of concentrated hydrochloric acid and thoroughly mix the contents with a glass-stirring rod. Spike the sample with surrogate(s).

7.3.2 The ultrasonic extraction of solids must be optimized for each type of sample. In order for the ultrasonic extractor to efficiently extract solid samples, the sample must be free flowing when the solvent is added. Acidified anhydrous sodium sulfate should be added to soils (normally 1:1), or any other solid that is not a free flowing sandy mixture, until a free flowing mixture is obtained.

7.3.3 Add 100 mL of methylene chloride/acetone (1:1 v/v – assign SRN) to the beaker. Perform ultrasonic extraction for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Allow the solids to settle.

7.3.4 Filter the extract into a 500-mL Erlenmeyer flask bottle using a Whatman 41 filter paper containing acidified sodium sulfate. The Erlenmeyer flask should contain 10 g of acidified sodium sulfate.

7.3.5 Ultrasonically extract the sample twice more using 100 mL of methylene chloride and the same ultrasonic conditions. Filter as in step 4 and combine the three organic extracts into the 500-ml Erlenmeyer flask containing the 10g of acidified sodium sulfate.

7.3.6 Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours.

NOTE: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2-hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight

7.3.7 Quantitatively transfer the entire contents of the flask, including sodium sulfate to the nitrogen blow-down flask using a funnel with a Whatman 41 filter paper. Rinse the inner walls of the flask into the filter funnel.

7.3.8 Evaporate the extract on using the Nitrogen evaporator to a volume of approximately 1-mL.

7.3.9 Dilute the extract with 1 mL of isooctane and 0.5 mL of methanol. Dilute to a final volume of 4 mL with diethyl ether. The sample is now ready for methylation with diazomethane

7.4 Esterification. Diazomethane derivatization - The bubbler method.

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

The bubbler method is suggested when small batches of samples (10 - 15) require esterification. The bubbler method works well with samples that have low concentrations of herbicides (e.g., aqueous samples) and is safer to use than the Diazald kit procedure.

The following precautions should be taken:

- ❑ Do not heat above 90oC - EXPLOSION may result.
- ❑ Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers –EXPLOSION may result.

7.4.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1 - 0.2 g of Diazald to the second test tube.

7.4.2 Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists.

7.4.3 The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1 - 0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane

7.4.4 There is sufficient KOH present in the original solution to perform a maximum of approximately 20 minutes of total esterification.

7.4.5 Remove the concentrator tube and seal it with a Neoprene or PTFE stopper. Store at room temperature in a hood for 20 minutes.

7.4.6 Destroy any unreacted diazomethane by adding 0.1 - 0.2 g of silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped.

7.4 7 Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube or transfer 1 mL of sample to a GC vial, and store refrigerated if further processing will not be performed immediately Extracts should be stored at 4oC away from light Most analytes are stable for 28 days.

7.5 Chromatographic conditions

7.5.1 System 1 carrier gas (Helium) flow rate: 5-10 ml/min

Temperature program

Initial temperature.	120°C, hold for 1 minutes
Program	120°C to 300°C at 8.5°C/min
Final temperature:	300°C hold for 8 minutes.

7.5.2 System 2 carrier gas (Helium) flow rate: 5-10 ml/min

Temperature program

Initial temperature:	90°C, hold for 1 minutes
Program:	90°C to 300°C at 11°C/min
Final temperature:	300°C hold for 0 minutes.

7.5.3 System 3 carrier gas (Helium) flow rate: 5-10 ml/min

Temperature program

Initial temperature·	120°C hold for 1 minutes
Program:	120°C to 300°C at 8 5°C/min
Final temperature:	300°C hold for 2 minutes

7.6 Data Processing – All data for organic instruments is acquired by the networked PC/Client acquisition software (ChromPerfect, Enviroquant..). Data files are then uploaded to the NT ChemServer for

processing and evaluation utilizing a networked version of the Target3 environmental data processing program. All processing methods/initial calibration are performed and maintained by the Target3 system.

7.7 Documentation

7.7.1 Daily Run Log. The samples analyzed for each analytical sequence are recorded on the daily run log. This log is identified by the analytical system and date analyzed and is used to record the analytical sequence prior to entry in the data acquisition system. A copy of the log(s) is included in the sequence package. Refer to Appendix E.

7.7.2 Sequence CheckList. This list is specific for this analytical method and is designed to ensure that all major QC elements of an analytical sequence are accounted for and evaluated. In addition, QC requirements for the preparation batch are also addressed. Refer to Appendix E.

7.8 Daily Instrument Maintenance. Due to the sensitivity of electron capture detectors (ECD), regularly scheduled maintenance is required to enable the analyst to obtain usable data as needed from the system. Maintenance should be performed daily, prior to the analysis of standards and samples

7.8.1 Daily maintenance consists of:

- ❑ Replace septa. Allow a maximum of 50 injections.
- ❑ Replace injection port seal and inlet sleeve.
- ❑ Cut approximate 1 to 2 inches from the head of the capillary column.
- ❑ Rinse the lumen of the inlet nut with hexane and blown dry with a micro-duster to remove any septum particles.
- ❑ Bake-out the GC at 260°C between sequences.

7.9 Retention Time Windows (RTW). The process of defining RTWs is detailed in the quality manual. By definition, this SOP requires that the default standard deviation of 0.01 minutes (window = 0.03 minutes) be used. RTW reports are generated periodically to monitor the analytical systems and ensure that the default value remains appropriate.

Note: The center of the absolute retention time window for each analyte is its retention time in the mid-concentration standard analyzed during the initial calibration.

7.10 Initial Calibration - The external standard procedure is used to calibrate the chromatographic system Prepare the calibration standards using the procedures outlined in section 5. Calibration procedures are detailed in the Quality Manual.

7.10.1 Calibrate the GC with an initial seven (7) point calibration using working standards as in Section 5.14. The lowest calibration standard (WS-1) is at or below the method quantitation limit (MQL). The highest calibration standard (WS-7) defines the upper linear range of the chromatographic system.

7.10.2 Note: When evaluating the initial calibration using Target 3 software, a minimum of five calibration levels must be used. If standard WS-1 is required for this method it must not be disabled. If the use of WS-1 does not meet initial calibration criteria, corrective action must be taken to allow the system to be calibrated with WS-1

7.10.3 Each calibration standard is directly injected via autosampler This technique will be used for all subsequent injections made on the chromatographic system The calibration factor (CF) is automatically calculated by the Target3 system.

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

7 10.3.1 Average CF Calibration. This is the first and best option that the analyst should consider and use whenever possible. To validate the initial calibration for this option, the percent relative standard deviation (RSD) of the CFs must be less than or equal to 20%.

7.10.3.2 Linear Regression If the %RSD of the average CF option is greater than 20% or at

$$\text{mean CF} \quad \overline{CF} \quad \frac{\sum CF}{n}$$

$$SD \quad \sqrt{\frac{\sum (CF_i - \overline{CF})^2}{n-1}} \qquad RSD \quad \frac{SD}{\overline{CF}} \times 100$$

the discretion of the analyst, a linear regression calibration may be used. The y-intercept must not be above the lowest calibration point in order to use this option.

7.10.3.3 Quadratic. Due to the nature and sensitivity of the ECD, this option is allowed specifically for the analysis of chlorinated herbicides This option may be used at the discretion of the analyst. The y-intercept must not be above the lowest calibration point in order to use this option.

7.10.3.4 The analyst should not force the line through the origin, but have the intercept calculated from the data points In addition, do not include the origin (0,0) as a calibration point. In order to be used for quantitative purposes, r must be greater than or equal to 0.99.

7.10 4 If the initial calibration curve does not meet the above criteria, a problem exists. Identify and correct the problem. Perform the initial calibration again. Sample analysis may not begin until the initial calibration has been validated.

7 11 Initial Calibration Verification (ICV). The initial calibration is verified as accurate by the analysis of an independent calibration verification standard. This standard is prepared independently of the ICAL from a second source. The ICV standard must meet method continuing calibration verification (CCV) criteria in order to validate the initial calibration.

7.12 As a rule, an initial calibration is performed for each analytical sequence. The ICV is analyzed after the last calibration standard.

7.13 Continuing Calibration Verification (CCV). The current initial calibration (CF and retention time) must be verified within each analytical sequence every 20 samples and at the end of the sequence. Verification is accomplished by the analysis of the mid-range standard WS-4. CCVs are analyzed in pairs (e.g. CV1A, CV1B).

7.13.1 Calculate the % difference

$$\% \text{ Difference} = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

where CFv is the calibration factor from the analysis of the verification standard, and CF is the mean calibration factor from the initial calibration.

7.13.1.1 The % difference for the calibration verification standard should not exceed ±15% for each analyte.

7.13.1.2 Section SW-846 also allows for the use of the averaged % difference of ***all calibrated analytes.*** The average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project. For Level III and IV data packages, CCV reports are provided along with a case narrative.

7.13.1.3 A maximum acceptance limit of 30% is used for individual compounds for the CCV when the grand mean approach is used.

7.13.1.4 SW-846 specifies that samples analyzed using external standards must be bracketed by periodic analyses of standards that meet the QC acceptance criteria (e.g., calibration and retention time). The results from these bracketing standards must meet the calibration verification criteria and the retention time criteria as listed above. However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >15%, and the analyte was not detected in any of the previous samples during the analytical shift, then the sample extracts do not need to be reanalyzed. The verification standard has demonstrated that the analyte would have been detected were it present.

7.13.2 All target analytes and surrogates should fall within previously established retention time windows.

7.13.3 If the CV does not meet the above criteria:

7.13.3.1 Evaluate the second CV for the failing analytes. If the second CV passes for those analytes, the sequence is valid.

7.13.3.2 If the second CV fails for the analytes, then samples analyzed before and after the failing CV may need re-analysis.

7.14 Gas chromatographic analysis

7.14.1 All extracts (standards and samples) are introduced into the gas chromatograph using automated direct injection. Samples are analyzed in a set referred to as an analytical sequence.

7.14.1.1 Sequences are initiated on the ChromPerfect data system. The information entered into the sequence file will be uploaded with the data file to the Target server Sequences procedures are detailed in the herbicide summary table.

7.14.1.2 The sequence is identified by the system identifier and the date of the analyses:

H2030901	
H2	= Herbicide System 2
030900	= Date of Analysis (03/09/00)
01	= First sequence of the day

7.14.1.3 Data files are defined by the sequence id plus the data file number:

H2030901.01R – 1st data file for this sequence.
H2030901.02R – 2end data file for this sequence

7.14.1.4 Typically an initial calibration followed by samples interspersed with mid-range calibration verification (CV) standards are analyzed. The sequence ends when the set of samples has been injected or when QC criteria has been exceeded (%D >15). The analytical sequence may begin with initial calibration verification followed by samples if the 15% criteria is met. A calibration verification standard must be analyzed after each group of 20 samples and at the end of the analytical sequence.

7.14.1.5 Detailed information concerning the analytical sequence is provided in the herbicide summary table.

7.14 2 A sequence checklist must be completed for each analytical sequence. This checklist summarizes the method requirements and allows the analyst to record information specific to the analytical sequence.

7.14.3 Extracts (sample and lab QC) are prepared in duplicate to allow the dual injection on both the primary and confirmation column.

7.14.3 1 100ul glass inserts are inserted in the autosampler vials. If dilutions are to be performed, no insert is used.

7.14.3.2 A portion of the sample extract is transferred to two (2) vials that are identically labeled. One will be placed in the autosampler for injection of the front column while the second will be placed to be injected on the back column.

7.14 4 Tentative identification of a single component analyte occurs when a peak from a sample extract falls within the absolute retention time window. Confirmation occurs when this analyte falls within the absolute retention time window for the second column. Target Form 10, Pesticide Dual Column Confirmation Check, is used to summarize the identified analytes (Appendix E).

7 14.4.1 Data for the primary analysis is reviewed initially for the tentative identification of an analyte.

7.14.4.2 If an analyte is identified in the primary, the confirmation analysis is reviewed for that analyte

7 14.4.3 Use the Target Form 10 perform evaluation as to whether an analyte is confirmed. Calculations are discussed in section 7.15

7.14.4.4 GC/MS confirmation may be used in circumstances where the concentration is high enough.

7.15 Calculations. All calculations are handled by the Target3 environmental sample processing software. Quantitation reports are generated for all samples (e.g. sample, blanks, controls…). These reports summarize the analytes identified, retention, area/height, on-column amount and final concentration adjusted for dilution and/or sample size.

7 15.1 Quantitation of single component analytes are determined by comparing the response in the sample to the CF from the initial calibration. Based on review of the initial calibration and calibration verifications, one column is assigned as primary and one is assigned as confirmation for the analytical sequence.

7 15.2 If the response of any confirmed analyte exceeds the upper calibration standard, the sample must be diluted and reanalyzed It is recommended that samples be diluted so that all peaks are on scale and have not exceeded the linear range of the detector. If peaks are off scale, the

judgment of the analyst is critical in determining if further dilutions are needed.

7.15.3 Water Samples

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

where:
A = Area (or height) of the peak for the analyte in the sample.
Vt = Total volume of the concentrated extract (ml) - default 10.
D = Dilution factor, if the sample or extract was diluted prior to analysis If no dilution was made, D = 1. The dilution factor is always dimensionless.
CF = Mean calibration factor from the initial calibration
Vi = Volume of the extract injected (µL) – default 1.
Vs = Volume of the aqueous sample extracted (ml) - default 1000.

Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

7.15.4 Solid Samples

$$\text{Concentration } (\mu g/kg) \quad \frac{(A_s)(V_t)(D)}{(\overline{CF})(V_i)(W_s)}$$

All values same as for water except:
Ws = Weight of sample extracted or purged (g). Either the wet weight or dry weight Unless otherwise specified, all soil results are reported on a dry weight basis Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

7.15.5 When sample results are confirmed (single or multi-component) the agreement between the quantitative results should be evaluated after the identification has been confirmed (e.g. Form 10). The relative percent difference (RPD) defines the difference between the two (2) results.

7.15 5.1 Results are reported, when possible, from the column assigned as primary.

7.15.5 2 If one result is significantly higher (e.g. >40%), check the chromatogram for any obvious sings of matrix interference such as overlapping peaks. If interference is obvious, the result should be reported from the second column.

7.15.5.3 If no anomalies are noted, then whenever possible, the high result should be reported. However, this may be precluded by the assignment of the column as confirmation.

7.16 Instrument Maintenance

7.16.1 Routine maintenance is an integral part of maintaining a productive quality analytical system throughout the laboratory. Instruments must be maintained at optimum performance to ensure the highest level of quality and sample throughput.

7.16.2 In addition, documentation of the maintenance in the instrument maintenance logbook will allow the analyst and supervisor to track the performance of the instrument, identify trends and minimize overall downtime.

7.16.2.1 Daily maintenance is described in section 7.8.

8.0 Quality Control/Quality Assurance/Corrective Action

8.1 Refer to the Quality Manual for QC procedures and evaluations to be employed for this method.

8.2 A summary of control limits and spike concentrations are provided in Appendix D to this SOP.

8.3 Corrective Actions are those actions performed to correct situations that are deemed adverse to data quality. Corrective actions are addressed in section 10 of the LQMP and in the SOP "Non-conformance and Corrective Action." Corrective actions are usually addressed within the procedure section of the analytical SOP. Examples of situations requiring corrective action:

8.3.1 Initial calibration does not meet criteria.

8.3.1.1 Review the initial calibration to see if any one (1) point appears as a significant outlier. This standard(s) may be re-analyzed and replaced in the initial calibration.

8.3.1.2 Compare calibration responses to previous calibrations to identify significant differences.

8.3 1 3 Review the calibration procedure and standards to ensure that they were prepared properly.

8.3.1.4 Evaluate the system and perform maintenance as necessary.

8.3.1.5 Perform the initial calibration again.

8.3.2 Calibration verification does not meet criteria.

8.3.2.1 Re-analyze the verification for the failing analytes. If these pass, the analytical sequence may continue. If the re-analysis fails for those analytes, the analytical sequence must be stopped and the system evaluated.

8.3.2.2 The use of the average percent difference for all calibrated analytes may be employed by the analyst based on discussion with the section supervisor and project manager.

8.3.3 Sample result above the high point in the initial calibration.

8.3.3.1 If the result is within 10% of the high point, the result is considered valid, flagged as "E – Exceeds calibration range" and reported. This result should be discussed in a Case Narrative.

8.3.3.2 If the result not within 10% of the high point, the result may be reported with approval from the project manager. This approval must take into account the data quality objectives of the project.

8.3.3.3 Re-analyze the sample at an appropriate dilution.

9.0 Data Validation

9.1 Refer to the Quality Manual for data validation procedures and guidelines.

10.0 Training & Training Validation

10.1 Refer to the Employee Training SOP for training procedures and guidelines.

11.0 Waste Disposal

11.1 Refer to the Waste Management Plan for waste disposal procedures.

12.0 Health and Safety

12.1 Refer to the Chemical Hygiene and Safety Plans for health and safety procedures and guidelines.

13.0 References

13.1 Solid Waste Manual, SW 846 Update III, December 1996.

13.2 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements, EM 200-1-3.

Appendix A
Detection Limits

Method Quantitation Limits			
		ug/L	ug/Kg
ANALYTE:	**CAS #**	**Water**	**Soil**
2,4-D	94-75-7	0 10	30.0
2,4-DB	94-82-6	0.10	20.0
2,4,5-TP(Silvex)	93-72-1	0.03	1.00
2,4,5-T	93-76-5	0.20	5.00
Dalapon	75-99-0	0.75	60.0
Dicamba	1918-00-9	0.80	20.0
Dichloroprop	120-36-5	0.10	10.0
Dinoseb	88-85-7	2.70	15.0
MCPA	94-74-6	180	510
MCPP	93-65-2	20	1000
Surrogates			
2,4-DCAA	19719-28-9		

Nominal Sample Size for Water: **1000mls**
Nominal Sample Size for Soil: **30g**
Nominal Final Volume: **10mls**

Appendix D
Control Limits

Recovery Limits			
ANALYTE:	**CAS #**	**Water**	**Soil**
2,4-D	94-75-7	20-150	20-150
2,4-DB	94-82-6	20-150	20-150
2,4,5-TP(Silvex)	93-72-1	20-150	20-150
2,4,5-T	93-76-5	20-150	20-150
Dalapon	75-99-0	20-150	20-150
Dicamba	1918-00-9	20-150	20-150
Dichloroprop	120-36-5	20-150	20-150
Dinoseb	88-85-7	20-150	20-150
MCPA	94-74-6	20-150	20-150
MCPP	93-65-2	20-150	20-150
Surrogates			
2,4-DCAA	19719-28-9	20-150	20-150

Appendix D

Spiking Solutions

Surrogate M-8150B-SS-PAK - Surrogate

Intermediate 2,4-Dichloriohenylacetic acid Spike 1ml per 250/1000mls or 30g

Final Volume = 10mls	FC ug/ml	FV 5ml (TCLP) ug/ml	FV ug/ml	FC 250mls ug/L	FC 1000mls ug/L	FC 30g ug/Kg
2,4-Dichlorophenylacetic Acid	2 5	0 50	0 20	10	2 5	83.3

LCS/MS - Current M-8150A-PAK - Targets Spike 1ml per 250/1000mls or 30g

Initial Conc ug/ml**	Final Volume = 10mls	FC ug/ml	FV 5ml (TCLP) ug/ml	FV ug/ml	FC 250mls ug/L	FC 1000mls ug/L	FC 30g ug/Kg
100	2,4-D	1 00	0 20	0.50	20.0	5 0	167
100	2,4-DB	1 00		0 50	20 0	5 0	167
100	2,4,5-T	1.00		0 50	20.0	5 0	167
100	2,4,5-TP(Silvex)	1 00	0 20	0 50	20 0	5.0	167
100	Dalapon	1 00		0 50	20.0	5 0	167
100	Dicamba	1 00		0.50	20 0	5 0	167
100	Dichloroprop	1 00		0 50	20 0	5 0	167
100	Dinoseb	1 00		0 50	20.0	5.0	167
10000	MCPA	100		50.00	2000 0	500.0	16667
10000	MCPP	100		50.00	2000 0	500 0	16667

LCS/MS - Current* HBM-8150A - Targets

Spike 1ml per 250/1000mls or 30

Initial Conc ug/ml*	Final Volume = 10mls	FC ug/ml	FV 5ml (TCLP) ug/ml	FV ug/ml	FC 250mls ug/L	FC 1000mls ug/L	FC 30g ug/Kg
100	2,4-D	1 00	0 20	0.10	4 0	1.0	33.3
100	2,4-DB	1 00		0 10	4.0	1 0	33 3
10	2,4,5-T	0 10		0 01	0 4	0 1	3 3
10	2,4,5-TP(Silvex)	0.10	0 02	0 01	0 4	0.1	3 3
250	Dalapon	2.50		0 25	10 0	2 5	83 3
10	Dicamba	0 10		0 01	0.4	0.1	3 3
100	Dichloroprop	1 00		0 10	4 0	1.0	33.3
50	Dinoseb	0 50		0 05	2 0	0 5	16.7
10000	MCPA	100		10	400	100	3333
10000	MCPP	100		10	400	100	3333

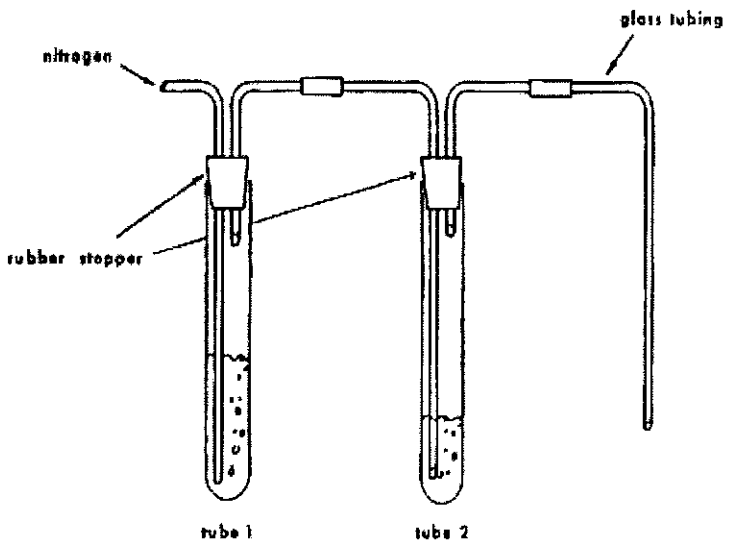
Appendix E

Run Log

Sequence Check List

Herbicide Dual Column Confirmation Check

Appendix F



Appendix G

Summary of Preparation Method

General Information

- Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure. The determination using pentafluorobenzylation is more sensitive and more prone to interferences from the presence of organic acids or phenols than by methylation.

- Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis. However, hydrolysis may result in the loss of dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids.

- The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water. Sodium sulfate must be acidified.

- Sample extracts should be dry prior to methylation or else poor recoveries will be obtained.

Ultrasonic extraction

1. Add 30 g (dry weight) of the well-mixed solid sample to a 250-mL beaker Adjust the pH to 2 with 2 drops of concentrated hydrochloric acid and thoroughly mix the contents with a glass-stirring rod. Spike the sample with surrogate(s).

2. The ultrasonic extraction of solids must be optimized for each type of sample. In order for the ultrasonic extractor to efficiently extract solid samples, the sample must be free flowing when the solvent is added. Acidified anhydrous sodium sulfate should be added to soils (normally 1:1), or any other solid that is not a free flowing sandy mixture, until a free flowing mixture is obtained.

3. Add 100 mL of methylene chloride/acetone (1:1 v/v – assign SRN) to the beaker. Perform ultrasonic extraction for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Allow the solids to settle.

4. Filter the extract into a 500-mL Erlenmeyer flask bottle using a Whatman 41 filter paper containing acidified sodium sulfate. The Erlenmeyer flask should contain 10 g of acidified sodium sulfate

5. Ultrasonically extract the sample twice more using 100 mL of methylene chloride and the same ultrasonic conditions. Filter as in step 4 and combine the three organic extracts into the 500-ml Erlenmeyer flask containing the 10g of acidified sodium sulfate.

6. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours

NOTE: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2-hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

7. Quantitatively transfer the entire contents of the flask, including sodium sulfate to the nitrogen blow-down flask using a funnel with a Whatman 41 filter paper. Rinse the inner walls of the flask into the filter funnel.

8. Evaporate the extract on using the Nitrogen evaporator to a volume of approximately 1 mL.

9. Dilute the extract with 1 mL of isooctane and 0.5 mL of methanol. Dilute to a final volume of 4 mL with diethyl ether. The sample is now ready for methylation with diazomethane.

Liquid/Liquid extraction

1. Using a graduated cylinder, transfer a 1-L sample aliquot to a 2-L separatory funnel. Spike the sample with the surrogate solution.

2. Add 250 g of NaCl to the sample, seal, and shake to dissolve the salt.

3. Add 17 mL of cold (4oC) 12 N sulfuric acid to the sample, seal, and shake to mix. Check the pH of the sample with pH paper. If the sample does not have a pH less than or equal to 2, adjust the pH by adding more acid.

   12N sulfuric acid – Slowly add 334 mls of concentrated sulfuric acid to 1 liter of organic free water. **NOTE: Always add acid to water.** This translates to 0.3mls of sulfuric acid per ml of organic free water. Assign a SRN and store in a labeled glass container.

4. Add 120-mL diethyl ether to the sample, seal, and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. Filter the ether using a funnel with Whatman 41 filter paper containing acidified sodium sulfate.

5. Remove the aqueous phase to a 2-L Erlenmeyer flask and collect the ether phase in a 500-mL Erlenmeyer flask containing approximately 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent.

6. Return the aqueous phase to the separatory funnel, add 60 mL of diethyl ether to the sample, and repeat the extraction procedure a second time, combining the extracts in the 500-mL Erlenmeyer flask Perform a third extraction with 60-mL diethyl ether in the same manner. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

   NOTE: The drying step is very critical to ensuring complete esterification. Any Moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

7. Quantitatively transfer the dried extract through a funnel with a Whatman 41 filter paper and collect the nitrogen-concentrating flask.

Esterification Diazomethane derivatization - The bubbler method

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

The bubbler method is suggested when small batches of samples (10 - 15) require esterification. The bubbler method works well with samples that have low concentrations of herbicides (e.g., aqueous samples) and is safer to use than the Diazald kit procedure. Extracts following hydrolysis may be difficult to handle by the bubbler method).

The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90E C - EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers – EXPLOSION may result.

1. Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1 - 0.2 g of Diazald to the second test tube.

2. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists.

3. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0 1 - 0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane.

4. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 minutes of total esterification.

5. Remove the concentrator tube and seal it with a Neoprene or PTFE stopper. Store at room temperature in a hood for 20 minutes.

6. Destroy any unreacted diazomethane by adding 0.1 - 0.2 g of silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped.

7. Adjust the sample volume to 10.0 mL with hexane Stopper the concentrator tube or transfer 1 mL of sample to a GC vial, and store refrigerated if further processing will not be performed immediately.

8. Extracts should be stored at 4oC away from light. Preservation study results indicate that most analytes are stable for 28 days;

Polychlorinated Biphenyls

Using SW-846 Method 8082

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

1.1 This method is used to determine the concentration of polychlorinated biphenyls. This SOP addresses the requirements of SW-846 methods 8000B (Revision 2 December 1996) and 8082 (Revision 0 December 1996). This method is applicable to the analysis of water, soil, liquid and solid samples.

1.2 Instrumentation: Dual capillary GC equipped with dual electron capture detectors (ECD) and autosampler

1.3 The method quantitation limit (MQL) is based on the lowest point in the initial calibration curve for a particular analyte. Detection limits (MDL, MQL, RL..) are detailed in Determination of MDL/MQL/RL. SOP.

1.4 Refer to LMP's Analytical Summary Table for applicable detection limits.

2.0 Summary of Method

2.1 Method 8082 is based on the solvent extraction of a sample (e.g. liquid/liquid or sonication) and subsequent concentration and clean up of the extract. The extract is then analyzed by capillary gas chromatography.

2.2 One thousand (1000) milliliters of water or 30 grams of soil is spiked with surrogate compounds and solvent extracted using Methylene Chloride for waters and 1:1 Methylene Chloride-Acetone for soils and the appropriate preparation method (see section 7). The extract is then concentrated and exchanged to hexane using a Nitrogen blow-down technique, cleaned up as necessary with sulfuric acid and/or potassium permanganate and analyzed by capillary GC.

2.3 LMP, Inc. utilizes simultaneous injection of the extract. The analytical systems available have dual autosamplers, dual injection ports, dual columns and dual detectors. This allows the acquisition of data from both the primary (A) and confirmation columns (B). Compound identification is based on qualitative and quantitative information from both columns.

2.4 This analytical method is based in part on *Methods 8000B and 8082 Solid Waste Manual SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition* and the *Shell for Analytical Chemistry Requirements" USACE version EM 200-1-3, 1 Feb 01*. Extraction and clean-up methods are referred to in this SOP.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by the extraction and analysis of method blanks. Specific selection of reagents and solvents may be necessary.

3.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

3.2.1 Common flexible plastics contain varying amounts of phthalate esters, which are easily extracted or leached from such materials during laboratory operations

3.2.2 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

3.2.3 Avoiding contact with any plastic materials can best minimize interferences from phthalate esters.

3.3 Method interferences are reduced by proper glassware cleaning procedures. Cleaning procedures are detailed in Organic Laboratory Glassware Cleaning Procedures SOP.

3.4 Method blanks must be extracted with each preparation batch to demonstrate that the system is free from method interferences.

3.5 High purity reagents must be used to minimize interference problems.

3.6 Contamination by carryover can occur whenever high-level and low-level samples are sequentially extracted. Extreme caution must be exercised whenever handling concentrated waste samples (e.g. product, solvent, and transformer oil).

4.0 Equipment and Apparatus

4.1 Gas chromatograph – Configuration 1 (This system is generally dedicated to the analysis of PCBs.)

4.1.1 Gas Chromatograph - Hewlett Packard 5890 Series II GC equipped with dual capillary column injection ports and dual electron capture detectors (ECD). The GC is equipped with a 100 place HP 7673

autosampler. Justice Innovations ChromPerfect software is utilized to acquire data where it is transferred to a central ChemServer and processed using Target analytical software.

4.1.2 Column 1 - 15 meter x 0.25-mm ID Phenomenex ZB-5 0.25 micron film thickness, catalog # FTG 6002-11

4.1.3 Column 2 – 15 meter x 0.25-mm ID Phenomenex ZB-35, 0.25 micron film thickness, catalog # FEG 6003-1

4.2 Gas chromatograph – Configuration 2 (This system is generally dedicated to the analysis of chlorinated pesticides but is applicable to PCB analysis.)

4.2.1 Gas Chromatograph - Hewlett Packard 6890 GC equipped with dual capillary column injection ports and dual electron capture detectors (micro ECD). The GC is equipped with a 100 place HP 7683 autosampler. Justice Innovations ChromPerfect software is utilized to acquire data where it is transferred to a central ChemServer and processed using Target analytical software.

4.2.2 Column 1 - 30 meter x 0.32-mm ID Restek RTx-CLPesticides 0.5 micron film thickness. Restek #11139

4.2.3 Column 2 – 30 meter x 0.32-mm ID Restek RTx- CLPesticidesII 0.25 micron film thickness. Restek #11324

5.0 Reagents and Standards

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Procedure (SVQAP).

5.3 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in *Chapter One of SW-846*.

5.4 Methylene Chloride – Fisher Scientific D151-4

5.5 Hexane – Fisher Scientific H303-4

5.6 Methanol – Fisher Scientific A454-4

5.7 Acetone – Fisher Scientific, GC Resolv

5.8 Stock calibration standards

5.8.1 Standards (targets and surrogates) are purchased as certified solutions from various vendors. The list of solutions, catalogue numbers and concentrations are listed in Table 2.

5.9 Intermediate Standards. Prepare the following standards in hexane:

5.9.1 Intermediate standards (targets and surrogates) are prepared from stock standards. Refer to Table 2 - Intermediate Standards

5.10 Working Standards. These standards are prepared from the intermediates listed in section 5.8 and are used to perform initial calibrations. Refer to Table 3 for the initial calibration dilution schedule.

5.11 Matrix spike and surrogate solutions are prepared from the same standards used to prepare the initial calibration. Refer to Table 2 for spike amounts and concentrations. QC limits are provided in Table 4.

5.12 The following considerations should always be followed in preparing all of the above standard solutions:

5.12.1 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Program (SVQAP).

5.12.2 Secondary dilution standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.12.3 Standards must be replaced after 6 months or sooner if comparison with the ICV standard indicates a problem.

5.12.4 Stock or neat solutions and standards must be stored in proper containers, away from light and should not be transferred from the original container. The date received, expiration date and any other pertinent information should be recorded in the Reagent Reference Log. The date received must also be recorded on the standard container, clearly visible to all analysts using it.

5.12.5 All intermediate and working solutions must be stored in light protected containers with Teflon lined caps at a temperature of 4 °C or less.

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

6.1.1 Refer to Sample Login Procedures SOP for guidance concerning containers, preservation and holding times.

6.2 Holding Times

6.2.1 Holding time for extraction is defined as the number of days from ***sample collection*** (e.g. sample date) to extraction.

6.2.2 Holding time for analysis is defined as the number of days from ***sample extraction*** in the laboratory to date injected/analyzed by the instrument

6.3 Aqueous samples are collected in one (1) liter amber bottles with Teflon lined caps No chemical preservation required. Soil samples are collected in 4 oz. or 8 oz. Teflon lined jars. Samples are stored at 4°C ± 2 from the time of collection. All water samples must be extracted within seven (7) days of collection. Soil samples must be extracted within fourteen (14) days of collection. All extracts, soil or water must be analyzed within 40 days of extraction.

7.0 Procedure

7.1 Samples are extracted based on matrix using one of the following sample extraction methods:

Method	Matrix	Introduction
3510	Water	Separatory Funnel Liquid-Liquid Extraction
3540	Soil / Solid	Soxhlet Extraction
3550	Soil / Solid	Ultrasonic Extraction
3580	Liquid / Solid	Waste Dilution
3665A	Extracts	Sulfuric Acid/Permanganate Cleanup

Sample preparation procedures are detailed within the above SOPs
In general, the following batch QC samples are required for each extraction batch (Table 6)

Method Blank (MB)

Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD). See section 5.10 for spiking solution information.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) – If enough sample is available.

7.2 Chromatographic conditions

7.2.1 System 1 carrier gas (Helium) flow rate 1-3 mL/min (10 psi)
Temperature program
Initial temperature: 120°C, hold for 1 minute
Program. 120°C to 300°C at 110°C/min
Final temperature 300°C hold for 2.64 minutes.

7 2 2 System 3 carrier gas (Helium) flow rate: 1.3mL/min
Temperature program
Initial temperature: 120°C, hold for 1 minute
Program 120°C to 300°C at 90°C/min
Final temperature 300°C hold for 4 minutes.

7.3 Data Processing – All data for organic instruments is acquired by the networked PC/Client acquisition software (ChromPerfect, Enviroquant..). Data files are then uploaded to the NT ChemServer for processing and evaluation utilizing a networked version of the Target environmental data processing program. All processing methods/initial calibration are performed and maintained by the Target system.

7.4 Documentation

7.4.1 Daily Run Log. The samples analyzed for each analytical sequence are recorded on the daily run log This log is identified by the analytical system and date analyzed and is used to record the analytical

sequence prior to entry in the data acquisition system. A copy of the log(s) is included in the sequence package.

7.4.2 Sequence CheckList. This list is specific for this analytical method and is designed to ensure that all major QC elements of an analytical sequence are accounted for and evaluated. In addition, QC requirements for the preparation batch are also addressed. Refer to Table 7.

7.5 Daily Instrument Maintenance. Due to the sensitivity of electron capture detectors (ECD), regularly scheduled maintenance is required to enable the analyst to obtain usable data as needed from the system. Maintenance should be performed daily, prior to the analysis of standards and samples.

7.5.1 Daily maintenance consists of:

- ❑ Replace septa. Allow a maximum of 50 injections.
- ❑ Replace injection port seal and liner.
- ❑ Cut approximate 1 to 2 inches from the head of the capillary column.
- ❑ Rinse the lumen of the inlet nut with hexane and blown dry with a micro-duster to remove any septum particles.
- ❑ Bake-out the GC at 325°C between sequences.

7.6 Retention Time Windows (RTW). By definition, this SOP requires that the default standard deviation of 0.01 minutes (window = 0.03 minutes) be used. RTW reports are generated periodically to monitor the analytical systems and ensure that the default value remains appropriate. RTWs are monitored for the same 3 to 5 major peaks used for initial calibration.

Note: The center of the absolute retention time window for each analyte is its retention time in the mid-concentration standard analyzed during the initial calibration.

7.7 Initial Calibration - The external standard procedure is used to calibrate the chromatographic system. Prepare the calibration standards using the procedures outlined in section 5..

7.7.1 Calibrate the GC with an initial six- (6) point calibration using working standards as in Section 5.9. The lowest calibration standard (WS-1) is below the method quantitation limit (MQL) of 0.5 µg/L for water and 35.0 µg/Kg for soil. The highest calibration standard (WS-6) defines the upper linear range of the chromatographic system.

7.7.2 The initial calibration is performed using a minimum of five (5) major peaks from Aroclor 1242 and a minimum of five (5) major peaks from Aroclor 1260.

7.7.3 Additional Multi-Component PCBs. A single mid-range standard is analyzed for each of the other Aroclors to aid in pattern recognition. If one of these PCBs is identified in a sample, the system is re-calibrated for that PCB with a minimum of three (3) standards. The extract is re-analyzed with the new calibration and quantitated. Calibrations for the multi-component PCBs are based on three (3) to five (5) major characteristic peaks.

7.7.4 Note: When evaluating the initial calibration using Target software, a minimum of five calibration levels must be used. Standard WS-1 is required for this method and must not be disabled. If the use of WS-1 does not meet initial calibration criteria, corrective action must be taken to allow the system to be calibrated with WS-1.

7.7.5 Each calibration standard is directly injected via autosampler. This technique will be used for all subsequent injections made on the chromatographic system. The calibration factor (CF) is automatically calculated by the Target system.

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

7.7.5.1 Average CF Calibration. This is the first and best option that the analyst should consider and use whenever possible. To validate the initial calibration for this option, the percent relative standard deviation (RSD) of the CFs must be less than or equal to 20%.

$$\text{mean CF} \quad \overline{CF} \quad \frac{\sum_{i=1}^{n} CF}{n}$$

7.7.5.2 Linear Regression. If the %RSD of the average CF option is greater than 20% or at the discretion

$$SD \quad \sqrt{\frac{\sum_{i=1}^{n} (CF_i \ \overline{CF})^2}{n \ 1}} \qquad RSD \quad \frac{SD}{\overline{CF}} \times 100$$

of the analyst, a linear regression calibration may be used. The y-intercept must not be above the lowest calibration point in order to use this option.

7.7.5.3 Quadratic. Due to the nature and sensitivity of the ECD, this option is allowed specifically for the analysis of PCBs. This option may be used at the discretion of the analyst. The y-intercept must not be above the lowest calibration point in order to use this option.

7.7.5.4 The analyst should not force the line through the origin, but have the intercept calculated from the data points. In addition, do not include the origin (0, 0) as a calibration point. In order to be used for quantitative purposes, R^2 must be greater than or equal to 0.995 for quadratic and 0.990 for linear.

7.7 6 If the initial calibration curve does not meet the above criteria, a problem exists. Identify and correct the problem. Perform the initial calibration again. Sample analysis may not begin until the initial calibration has been validated.

7.8 Continuing Calibration Verification (CCV) The current initial calibration (CF and retention time) must be verified within each analytical sequence every 20 samples and at the end of the sequence. Verification is accomplished by the analysis of the mid-range standard WS-4. When regression analysis is performed, % Drift is calculated. Likewise, the use of % Difference will be used when the initial calibration is based on % RSD values.

7.8.1 To calculate the % Difference

$$\% \text{ Difference} \quad \frac{CF_v \ \overline{CF}}{\overline{CF}} \times 100$$

where CFv is the calibration factor from the analysis of the verification standard, and CF is the mean calibration factor from the initial calibration.

7.8.1.1 The % difference for the calibration verification standard should not exceed ±15% for each analyte.

7.8.1.2 Section SW-846 also allows for the use of the averaged % difference of ***all calibrated analytes.*** The average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project. For Level III and IV data packages, CCV reports are provided along with a case narrative.

7 8.1.3 SW-846 specifies that samples analyzed using external standards must be bracketed by periodic analyses of standards that meet the QC acceptance criteria (e g., calibration and retention time). The results from these bracketing standards must meet the calibration verification criteria and the retention time criteria as listed above. However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >15%, and the analyte was not detected in any of the previous samples during the analytical shift, then the sample extracts do not need to be reanalyzed. The verification standard has demonstrated that the analyte would have been detected were it present

7.8.2 All target analytes and surrogates should fall within previously established retention time windows.

7.8.3 If the CV does not meet the above criteria:

7.8.3.1 Evaluate the second CV for the failing analytes. If the second CV passes for those analytes, the sequence is valid.

7.8.3.2 If the second CV fails for the analytes, then samples analyzed before and after the failing CV may need re-analysis.

7.9 Gas chromatographic analysis

7.9.1 All extracts (standards and samples) are introduced into the gas chromatograph using automated direct injection. Samples are analyzed in a set referred to as an analytical sequence.

7.9.1.1 Sequences are initiated on the ChromPerfect data system. The information entered into the sequence file will be uploaded with the data file to the Target server.

7.9.1.2 The sequence is identified by the system identifier and the date of the analyses:

P3030901	
P3	= PCB System 1
0309	= Date of Analysis (03/09)
01	= First sequence of the day

7.9.1.3 Data files are defined by the sequence id plus the data file number:

P3030901.01R – 1st data file for this sequence.
P3030901.02R – 2end data file for this sequence.

7.9.1.4 Typically an initial calibration followed by samples interspersed with mid-range calibration verification (CV) standards are analyzed. The sequence ends when the set of samples has been injected or when QC criteria has been exceeded (%D >15). The analytical sequence may begin with initial calibration verification followed by samples if the 15% criteria is met A calibration verification standard must be analyzed after each group of 20 samples and at the end of the analytical sequence.

7.9.2 A Sequence Checklist (Table 7) must be completed for each analytical sequence This checklist summarizes the method requirements and allows the analyst to record information specific to the analytical sequence.

7.9 3 Extracts (sample and lab QC) are prepared in duplicate to allow the dual injection on both the primary and confirmation column.

7.9.3.1 200uL glass inserts are inserted in the autosampler vials. If dilutions are to be performed, no insert is used.

7.9.3.2 A portion of the sample extract is transferred to two (2) vials that are identically labeled. One will be placed in the autosampler for injection on the front column, while the second will be placed for injection on the back column.

7.9.4 Identification of multi-component analytes is based on the characteristic fingerprint retention time and shape of the indicator peaks. Three (3) to five (5) major peaks are selected for use in qualitative and quantitative identification.

7.9.4.1 Data for the primary analysis is reviewed initially for the tentative identification of the analyte.

7.9.4.2 If an analyte is identified in the primary, the confirmation analysis is reviewed for that analyte.

7.9.4.3 Use the Target Form 10 to perform an evaluation as to whether an analyte is confirmed.

7.9.4.4 GC/MS confirmation may be used in circumstances where the concentration is high enough.

7.10 Calculations. All calculations are handled by the Target environmental sample processing software. Quantitation reports are generated for all samples (e.g. sample, blanks, controls). These reports summarize the analytes identified, retention, area/height, on-column amount and final concentration adjusted for dilution and/or sample size.

7.10.1 Quantitation of analytes are determined by comparing the response in the sample to the CF from the initial calibration. Based on review of the initial calibration and calibration verifications, one column is assigned as primary and one is assigned as confirmation for the analytical sequence.

7.10.2 Quantitation of Aroclors other than 1242 and 1260 is accomplished according to the following.

7.10.2.1 Upon identification of a multi-component analyte, the sample must be re-analyzed after a minimum three (3)-point initial calibration.

7.10.2.2 Quantitation is performed by comparing the response in the sample of the 3 to 5 characteristic peaks to the CF from the initial calibration of the *same characteristic peaks.*

7.10.2.3 Based on review of the initial calibration and calibration verifications, one column is assigned as primary and one is assigned as confirmation for the analytical sequence.

7.10.3 If the response of any confirmed analyte exceeds the upper calibration standard, the sample must be diluted and reanalyzed. It is recommended that samples be diluted so that all peaks are on scale and have not exceeded the linear range of the detector If peaks are off scale, the judgment of the analyst is critical in determining if further dilutions are needed.

7 10.4 Water Samples

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

where:

A = Area (or height) of the peak for the analyte in the sample.
Vt = Total volume of the concentrated extract (mL) - default 10.
D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.
CF = Mean calibration factor from the initial calibration
Vi = Volume of the extract injected (µL) – default 1.
Vs = Volume of the aqueous sample extracted (mL) - default 1000.

Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

7 10 5 Solid Samples

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(V_t)(D)}{(\overline{CF})(V_i)(W_s)}$$

All values same as for water except.
Ws = Weight of sample extracted or purged (g) Either the wet weight or dry weight. Unless otherwise specified, all soil results are reported on a dry weight basis Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

7 10.6 When sample results are confirmed (single or multi-component) the agreement between the quantitative results should be evaluated after the identification has been confirmed (e.g. Form 10). The relative percent difference (RPD) defines the difference between the two (2) results. The RPD must be less than 40% when at least one result is greater than the quantitation limit.

7.10 6.1 Results are reported, when possible, from the column assigned as primary.

7.10 6.2 If one result is significantly higher (e.g. >40%), check the chromatogram for any obvious signs of matrix interference such as overlapping peaks If interference is obvious, the result should be reported from the second column.

7 10.6.3 If no anomalies are noted, then whenever possible, the high result should be reported. However, this may be precluded by the assignment of the column as confirmation.

7.11 Instrument Maintenance.

7.11.1 Routine maintenance is an integral part of maintaining a productive quality analytical system throughout the laboratory. Instruments must be maintained at optimum performance to ensure the highest level of quality and sample throughput.

7.11.2 In addition, documentation of the maintenance in the instrument maintenance logbook will allow the analyst and supervisor to track the performance of the instrument, identify trends and minimize overall downtime.

7.11.2.1 Daily maintenance is described in Section 7.5.

8.0 Quality Control/Quality Assurance/Corrective Action

8.1 A summary of control limits and spike concentrations are provided in Table 4.

8.2 Corrective Actions are those actions performed to correct situations that are deemed adverse to data quality. Corrective actions are addressed in section 10 of the LQMP and in the Non-Conformance and Corrective Action SOP. Corrective actions are usually addressed within the procedure section of the analytical SOP. Examples of situations requiring corrective action:

8.2.1 Initial calibration does not meet criteria.

8.2.1.1 Review the initial calibration to see if any one (1) point appears as a significant outlier. This standard(s) may be re-analyzed and replaced in the initial calibration.

8.2.1.2 Compare calibration responses to previous calibrations to identify significant differences.

8.2.1.3 Review the calibration procedure and standards to ensure that they were prepared properly.

8.2.1.4 Evaluate the system and perform maintenance as necessary.

8.2.1.5 Perform the initial calibration again.

8.2.2 Calibration verification does not meet criteria.

8.2.2.1 Re-analyze the verification for the failing analytes. If these pass, the analytical sequence may continue. If the re-analysis fails for those analytes, the analytical sequence must be stopped and the system evaluated.

8.2.2.2 The use of the average percent difference for all calibrated analytes may be employed by the analyst based on discussion with the section supervisor and project manager.

8.2.3 Sample result above the high point in the initial calibration.

8.2.3.1 If the result is within 10% of the high point, the result is considered valid, flagged as "E – Exceeds calibration range" and reported. This result should be discussed in a Case Narrative.

8.2 3.2 Re-analyze the sample at an appropriate dilution

9.0 Training and Training Validation

Employee training on documented procedures may be found in the Employee Training SOP. Demonstration of the employee's training in the specific procedures involved in this method may be found in the Training Documents Log This documentation includes all in-house and outside training received and include items such as proficiency testing and information on performance testing results. A Demonstration of Capability is on file for each analyst performing the test.

10.0 Data Validation

Refer to the Data Reduction and Review SOP.

11.0 Health and Safety

Refer to the Chemical Hygiene Plan and Laboratory Safety Plan SOPs.

12.0 Waste Disposal and Pollution Management

Refer to the Waste Management Plan SOP for waste disposal procedures.

13.0 References

- LMP's Definitions, Acronyms, Symbols and Abbreviations Policy
- Solid Waste Manual, SW846 Update III, December 1996, Method 8082.
- U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical EM 200-1-3, 1 Feb 01.
- EPA, Methods for Chemical Analysis of Water and Wastes, EPA –600/4-79-020, March 1983.
- NELAC, Quality Systems, Revision 15, May 25, 2001.
- NELAC, Program Policy and Structure, Revision 13, June 29, 2000.
- 40 CFR Part 136 Appendixes A.
- EPA Guidance for Preparing Standard Operating Procedures (SOPs), EPA QA/G-6, EPA/240/B-01/004, March 2001
- USEPA 2185 – Good Automated Laboratory Practices
- USEPA 600/4-79-020, Methods for Chemical Analysis of Water and Wastes, March 1983.
- OSHA Laboratory Standard, 29 CFR 1910.1450.
- OSHA Compliance Guide, Kirk H. Ray, 8th Edition.
- *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.
- Laboratory Safety in Practice. A Comprehensive Compliance Program and Safety Manual.
- *"Safety in Academic Chemistry Laboratories"*, American Chemical Society Publication, Committee on Chemical Safety.
- *"Carcinogens – Working with Carcinogens"*, Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

Tables

Table 1

Method Quantitation Limits

ANALYTE	CAS #	Water µg/L	Soil µg/Kg
Aroclor 1016	12674-11-2	0.50	35.0
Aroclor 1221	11104-28-2	0.50	35.0
Aroclor 1232	11141-16-5	0.50	35.0
Aroclor 1242	53469-21-9	0.50	35.0
Aroclor 1248	12672-29-6	0.50	35.0
Aroclor 1254	11097-69-1	0.50	35.0
Aroclor 1260	11096-82-5	0.50	35 0
Surrogates			
Tetrachloro-m-xylene (TMX)	877-09-8	31- 96	39-130
Decachlorobiphenyl (DCB)	2051-24-3	34-115	64-154

Nominal Sample Size for Water	1000mL
Nominal Sample Size for Soil:	30g
Nominal Final Volume	10mL

Table 2

Standard Solutions

Solution	Description	Use	Conc ug/ml	Solvent	Vendor
C-216S-H-10X	Aroclor 1016	ICAL	1,000	Isooctane	Accustandard
C-221S-H-10X	Aroclor 1221	ICAL	1,000	Isooctane	Accustandard
C-232S-H-10X	Aroclor 1232	ICAL	1,000	Isooctane	Accustandard
C-242S-H-10X	Aroclor 1242	ICAL/LCS/MS	1,000	Isooctane	Accustandard
C-248S-H-10X	Aroclor 1248	ICAL	1,000	Isooctane	Accustandard
C-254S-H-10X	Aroclor 1254	ICAL	1,000	Isooctane	Accustandard
C-260S-H-10X	Aroclor 1260	ICAL/LCS/MS	1,000	Isooctane	Accustandard
C-262S-H-10X	Aroclor 1262	ICAL	1,000	Isooctane	Accustandard
C-268S-H-10X	Aroclor 1268	ICAL	1,000	Isooctane	Accustandard
Z-008S-M	Pack of all of the above		1,000	Isooctane	Accustandard
PCB-1242H	Aroclor 1242	ICV	1,000	Hexane	Protocol
PCB-1260H	Aroclor 1260	ICV	1,000	Hexane	Protocol
4-4806	Aroclor 1242 (LCS/MS)		1,000	Isooctane	Supelco
4-4809	Aroclor 1260 (LCS/MS)		1,000	Isooctane	Supelco
C-242S-H-10X-PAK	Pack of 5 of 1242 (LCS/MS)		1,000	Isooctane	Accustandard
C-260S-H-10X-PAK	Pack of 5 of 1260 (LCS/MS)		1,000	Isooctane	Accustandard
ISM-320	Surrogate DCB/TMX		200	Acetone	Ultra
CLP-032R	Surrogate DCB/TMX		200	Acetone	Accustandard

Intermediates

PCBICAL1	ICAL PCB	PCB Intermediate - Hexane	1ml of stock solution to 10mls of hexane = 100 ug
PCBSURICAL1	ICAL Surrogate	Surrogate Intermediate - Hexane	0.5ml of stock solution to 10mls of hexane = 10 u
PCBSPK1	LCS/MS Solution	1242/1260 Intermediate - Hexane	1ml of 4-4806 plus 1ml of 4-4809 to 10mls of hex

Table 3

Initial Calibration Dilution Schedules

Analyte	Intermedial Nominal µg/mL	WS-1 1 µL	WS-2 5 µL	WS-3 12.5 µL	WS-4 25 µL	WS-5 37.5 µL	WS-6 50 µL
1242/1260	1000	0.020	0.100	0.250	0.500	0.750	1.000
1016	1000	0.020	0.100	0.250	0.500	0.750	1 000
1221	1000	0 020	0.100	0.250	0.500	0.750	1.000
1323	1000	0.020	0.100	0.250	0.500	0.750	1.000
1248	1000	0.020	0.100	0.250	0.500	0.750	1 000
1254	1000	0.020	0.100	0.250	0.500	0 750	1.000
1262	1000				0 500		
1268	1000				0.500		

Analyte	Intermedial Nominal µg/mL	WS-1 5 µL	WS-2 25 µL	WS-3 62.5 µL	WS-4 125 µL	WS-5 187 5 µL	WS-6 250 µL
TMX/DCB	20	0.002	0.010	0 025	0.050	0.075	0.100

Working standards are prepared by adding the specified µL of PCB/Surrogate to 50 mL of Hexane.

Table 4

Control Limits

Recovery Limits

ANALYTE	Water	Soil
Aroclor 1016	25-125	25-125
Aroclor 1221	25-125	25-125
Aroclor 1232	25-125	25-125
Aroclor 1242	25-125	25-125
Aroclor 1248	25-125	25-125
Aroclor 1254	25-125	25-125
Aroclor 1260	25-125	25-125
Surrogates		
Tetrachloro-m-xylene (TMX)	31- 96	20-122
Decachlorobiphenyl (DCB)	34-115	17-141

Table 5

Spiking Solutions

Water/Soil Surrogate Solution	**PCB Surrogate**	200µL of ISM/320 or CLP-032R into 100mL of MeOH = 0.40µg/mL FC = 0.4µg/mL. Spike 1mL per 1000mL or 30g (FV=10mL)		
			FV	**FC**
		Water	0.04µg/mL	0.4µg/L
		Soil	0.04µg/mL	13.3µg/Kg
Spike Solution	**PCB Spike**	5mL of PCBSPK1 into 100mL of Acetone = 5µg/mL FC = 5. 0µg/mL. Spike 1mL per 1000mL or 30g (FV=10mL)		
			FV	**FC**
		Water	0 04µg/mL	0.4µg/L
		Soil	0.04µg/mL	13.3µg/Kg
Oil Surrogate Solution	**PCB Surrogate**	200 µL of ISM/320 or CLP-032R into 100mL of Hexane = 0.40µg/mL FC = 0.4µg/mL Spike 1mL per 0 5g (FV=10mL)		
			FV	**FC**
		Oil	0.04µg/mL	800µg/Kg

FV = Final volume
FC = Final concentration

Table 6

Summary of Measurement quality objectives for Method 8082

Quality control element	Target Analyte / Surrogate
Initial Calibration	R^2 0.995, % RSD 20%, R^2 0.990
ICV	% Rec = 85% - 115%
CCV	% D 15%
MB	Analytes < one-half MRL
LCS	Water & Soil : % Rec = See Analytical Summary Table
MS	Water & Soil : % Rec = See Analytical Summary Table
MSD/MD	RPD 20%
Surrogates	% Interference-Free Matrix: Water & Soil : % Rec = See Analytical Summary Table
Target Analyte Confirmation	RPD 40%

Table 7

GC PCB Method 8082 Sequence Check List

HBN:_____
Sequence ID : _____System ID:_____ Date:_____ Analyst:_____
Column ID: Primary / Confirmation Column Description: _____ Supervisor:_____
Applicable LMP Order Nos. for this sequence:

_____ _____ _____ _____
_____ _____ _____ _____

1. Initial Calibration _____
   RSD of analytes <=20% may use average RF.
   RSD of analytes >=20% or analyst discretion, use linear regression (r^2>=0.99)

Calibration Verification – Beginning/Every 20th Sample / Ending. Note only that %D that affects data.
%Difference <15% or Average %Difference of All Analytes <15%.

CV w/File #	PCB-1242	PCB-1260	DCB	TMX	Average
1A					
1B					
2A					
2B					
3A					
3B					

Method Blanks – Note results for positive results. Flag final results as **B – Detected in Blank.**
1 per 20 samples per matrix.

Method Blank				

Laboratory Control Samples – Note failures only. 1 per 20 samples per matrix. Duplicate LCS when no MS/MSD available.

LCS/LCSD				

Matrix Spike/Matrix Spike Duplicate – 1 per 20 samples per matrix.
Notes:_____

Standard Operating Procedure For Separatory Funnel Liquid-Liquid Extraction SW-846 Method 3510C

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 Summary of Method

2.1 A measured volume of sample, usually 1 liter, at a specified pH (refer to Table 3), is serially extracted with methylene chloride using a separatory funnel This method is applied to *all liquid/liquid extractions* regardless of the analytical method except Method 8151 (Herbicides) The difference will be in the pH of the extraction (Table 3), the QC solutions to be added to each sample and the exchange solvent if required.

2.2 The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used (refer to Table 3 for appropriate exchange solvents).

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing equipment may yield artifacts of interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and solvents may be necessary.

3.1.1 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.1.2 Glassware contamination can result in analyte degradation. Detergent residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorus pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem. Chromic acid that is not completely rinsed will cause similar problems with analyte degradation and should be carefully rinsed to avoid this problem.

3.1.3 Refer to Organic Laboratory Glassware Cleaning Procedure SOP

4.0 Equipment and Apparatus

4.1 Logbooks

Maintenance logbooks will contain, as applicable, Instrument Maintenance Schedule and Requirements, Daily Maintenance, Weekly Maintenance, Monthly Maintenance, and Typical Problems/Solutions.

4.2 Refer to Table 1 for a listing of Equipment and supplies.

5.0 Reagents and Standards

5.1 Policy

5.1 1 ACS reagent grade chemicals shall be used in all tests. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5 1 2 Organic-free reagent water – Refer to Reagent and Standard Solutions Validation SOP.

5 1.3 Refer to Table 2 for a listing of reagents and standards.

5.1.4 Sodium sulfate (granular, anhydrous) is used with filter paper to help prevent water from getting through the filter and to assist in breaking up emulsions It is placed in the oven at 170°C in its original container and left overnight to dry. It is then moved to a dessicator until needed. The sodium sulfate is pre-rinsed with Methylene chloride prior to use.

5.2 Solutions

5.2.1 Sodium hydroxide solution (5N), NaOH: Weigh 400 g of sodium hydroxide and transfer to a 2000mL volumetric flask (glass) with a Teflon-coated stir bar. Next, add 1000mL of deionized water using a 1000mL graduated cylinder. Using a glove, mix the sodium hydroxide pellets because the volumetric flask will become extremely hot. Continue to mix until all of the pellets are dissolved. Bring the solution to volume by adding deionized water and the solution becomes clear and room temperature.

5.2.2 Hydrochloric acid solution (HCl, 1:1): In a 1000mL volumetric flask add 500mL deionized water, then slowly add 500mL of concentrated HCl. The solution will get warm. Place a top on the flask and allow it to cool. Bring up to volume with deionized water and mix well before use.

5.3 Standards

5.3.1 Spiking solutions (e.g., those used for LCS/LCSD, MS/MSD, surrogates, internal standards) are referenced specifically in the analytical method. This will include information related to specific analytes being spiked, the concentrations, amount added, preparation schedule, expiration and storage. Refer to Table 4 for a listing.

6.0 Sample Preservation and Containers

6.1 Samples are stored in the walk-in refrigerator at 4 °C ± 2. Samples are located by the date received as noted on the LMP ID label.

6.2 Holding times are very important and samples must be extracted regardless of when the samples arrive. The holding times are method and matrix specific. Consult the analytical method for details.

7.0 Procedure

7.1 All samples have a due date; sample extracts should delivered to the analytical laboratory at least 2 or 3 days in advance of the due date, if possible.

7.2 The scheduling of samples depends on the client, number of samples, due date and holding times and personnel on a day-to-day basis.

7.3 Samples must be at room temperature before proceeding with extraction. Usually, the process of allowing the samples to reach room temperature will also allow the solids in the sample to settle.

7.4 Samples should be lined-up in front of the separatory funnels. Separatory funnels should be clearly labeled with the LMP Order # or other sample ID (Blank, LCS, MS/MSD) with a black indelible marker.

7.5 Mark the meniscus of each sample on the outside of the sample container. All sample containers must be marked in order to determined the volume after extraction by filling the original container with tapwater or sample water and measuring the volume with a Class A graduated cylinder. This volume will be documented on the appropriate extraction sheet for the corresponding sample.
Note: Technician observation is extremely important at this stage. Actual sample size used is critical to the success of the analysis. Consult with your supervisor on any sample that does not appear typical, e.g. strong solvent odor or high amounts of solids.

7.6 Transfer the entire contents of the sample to the separatory funnel when applicable If high concentrations are anticipated, a smaller volume may be used and add deionized water to bring volume to one liter.. The following procedure must be followed when a smaller volume of sample is used

7.6.1 Select an appropriate size graduated cylinder based on the amount of sample to be used.

7.6.2 Using a black indelible marker, label the base of the cylinder with the LMP Sample ID.

7.6.3 Measure the required amount of sample into the graduated cylinder.

7.6.4 Transfer the sample from the graduated cylinder to the 2 L separatory funnel. DO NOT ***Discard or rinse*** the graduated cylinder at this time and add deionized water to bring volume to one liter.

7.7 Check the pH of the sample with intermediate-range pH paper. The initial pH is recorded on the extraction sheet.

7.8 QC solutions (e.g. surrogates, controls, and spikes) are added to samples in order to monitor the extraction process. As per Method 3500, add the appropriate amount of the surrogate standards to all samples, spikes, and blanks (See the appropriate analytical method for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add the appropriate

amount of the matrix-spiking standard. See the Appendix for descriptions of the different type solutions and their uses.

7.9 An oversight person will double-check the technician to make sure the surrogate and spike, which is clearly labeled, is being used for the appropriate test.

7.10 After adding the surrogate solution and if necessary, adjust the pH to that indicated in Table 3 in the Appendix for the specific determinative method that will be used to analyze the extract.

7.11 Add the 1st aliquot of extracting solvent (60mL) to the empty sample container or graduated cylinder if smaller volume used. Replace the bottle cap, mix and transfer it quantitatively to the separatory funnel.

7.12 Seal and shake the separatory funnels vigorously with periodic venting to release excess pressure. Place the separatory funnels in the automatic shaker and set the timer for 2 minutes. Vent the separatory funnel periodically to remove any excess pressure that has built up
Note: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to prevent unnecessary exposure of the analyst to solvent vapors. Venting must be performed as necessary during automatic shaking as well.

7.13 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques, such as centrifugation, to complete the phase separation

7.14 The following steps are taken to break up an emulsion. Drain the emulsion into a centrifuge bottle or 40mL vial and load extracts into the centrifuge machine #1 or #2. Make sure they are properly balanced and labeled. Spin samples at a speed of 30 rpm for 5-10 minutes. Pour the solvent layer through a filter funnel with a #41 filter paper with sodium sulfate or glass wool and sodium sulfate into a 250/500mL Erlenmeyer flask.

7.14.1 Pour the emulsive layer back into the separatory funnel and repeat the above steps, if necessary. Emulsions usually break up after the first or second shake.

7.14.2 Drain the emulsion into a 250mL beaker and add sodium sulfate and some methylene chloride using a glass-stirring rod to break up the sodium sulfate. Sodium sulfate gets hard when added to an emulsion. Continue stirring until it breaks up.

7.14.3 Filter into a 250/500mL Erlenmeyer flask.

7.14.4 The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through filter paper and sodium sulfate, centrifugation, or other physical methods Collect the solvent extract in an Erlenmeyer flask or centrifuge bottle

7.15 Repeat the extraction two more times using fresh portions of solvent. Combine the three solvent extracts.

7.16 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 3. Serially extract three times with 60mL of methylene chloride, as outlined above Collect and combine the extracts and label the combined extract appropriately.

7.17 If performing GC/MS analysis (Method 8270C), the acid and base/neutral extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid and base/neutral extracts may be preferable (e.g if for regulatory purposes the presence or absence of specific acid/neutral or base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.18 An Extraction Logbook will be maintained.

7.19 Rapid-Vap Nitrogen (N_2) Concentration

7.19.1 At the time that samples are ready for concentration, pour extract into the Rapid Vap N_2 flasks. The evaporator should be set as follows:

Soil Samples	
BNA	
Time	approx. 40 minutes
Temp	50 °C
Vortex	50
Final volume	1mL Methylene chloride
Pest & PCB's (Water and Soil)	
Time	approx. 40 minutes
Temp.	50 °C
Vortex	50
Final volume	10mL exchanged to Hexane
BNA Water Samples	
Time	approx. 60 minutes
Temp	50 °C
Vortex	50
Final volume	1mL Methylene chloride
For DRO Concentrations (Water and Soil)	
Time	approx. 40 minutes
Temp	50°C
Vortex	50
Final volume	1mL Methylene chloride

CAUTION: When the volume of solvent is reduced below 1mL, semi-volatile analytes may be lost.

7.19.2 The Rapid-Vap N_2 Evaporation System should be already on at a set temperature of 50°C and a Vortex speed of 50%.

7.19.3 Place the sample tubes in the Rapid-Vap at a volume not to exceed 250mL due to possible contamination. Lower the lid and nitrogen will begin to blow into the sample and concentration will begin.

7.19.4 Set the timer and continue to concentrate the samples until a final volume that is acceptable for the specific method is obtained. This volume is usually 1mL. If the sample concentrates below the 1mL mark let the Rapid-Vap flask cool, then add the preferred solvent to the sample and bring it to volume.

7.19.5 If you need to exchange the solvent, concentrate the extract down to 2mL, add at least 30mL of preferred solvent and re-concentrate down to the desired final volume. Remove from the Rapid-Vap until you are ready to transfer to 2mL vials.

7.19.6 Transfer the extract from the sample tube to the vial. If the final volume is 0.01 to 4mL, use a serological pipette and pipette bulb to draw the solvent to the desired final volume for the appropriate test.

7.19.7 If the final volume is 5mL or above pour the extract into a graduated cylinder and bring it up to the volume which is required for the test.

7.19.8 The extract obtained may now be analyzed for analyte content using a variety of organic techniques. If analysis of the extract or any step in the extraction procedure will not be performed immediately, stopper the concentrator tube or cover the flask with aluminum foil and store refrigerated. If the

extract will be stored longer than 2 days it should be transferred to a vial with a Teflon-lined screw cap or crimp top, and labeled appropriately.

8.0 Quality Control/Quality Assurance/Corrective Action

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same procedures as those used upon actual samples

8.2 Refer to *SW846 Method 3500* for extraction and sample preparation procedures.

9.0 Training and Training Validation

9.1 Employee training on documented procedures may be found in the Employee Training SOP. Demonstration of the employee's training in the specific procedures involved in this method may be found in the Training Documents Log This documentation includes all in-house and outside training received and include items such as proficiency testing and information on performance testing results. A Demonstration of Capability is on file for each analyst performing the test.

10.0 Data Validation

10.1 Refer to the Data Reduction and Review SOP

11.0 Health and Safety

11.1 Refer to the Chemical Hygiene Plan and Laboratory Safety Plan SOPs.

12.0 Waste Disposal and Pollution Management

12.1 Refer to the Waste Management Plan SOP for waste disposal procedures

13.0 References

13.1 LMP's Definitions, Acronyms, Symbols and Abbreviations Policy

13.2 Solid Waste Manual, SW846 Update III, December 1996.

13.3 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements EM 200-1-3,1 Feb 01.

13.4 EPA, Methods for Chemical Analysis of Water and Wastes, EPA –600/4-79-020, March 1983.

13.5 NELAC, Quality Systems, Revision 15, May 25, 2001

13.6 NELAC, Program Policy and Structure, Revision 13, June 29, 2000

13.7 40 CFR Part 136 Appendix A.

13.8 EPA Guidance for Preparing Standard Operating Procedures (SOPs), EPA QA/G-6, EPA/240/B-01/004, March 2001

13.9 USEPA 2185 – Good Automated Laboratory Practices

13.10 USEPA 600/4-79-020, Methods for Chemical Analysis of Water and Wastes, March 1983.

13.11 OSHA Laboratory Standard, 29 CFR 1910.1450

13.12 OSHA Compliance Guide, Kirk H. Ray, 8th Edition.

13.13 *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986

13.14 Laboratory Safety in Practice. A Comprehensive Compliance Program and Safety Manual.

13.15 *"Safety in Academic Chemistry Laboratories"*, American Chemical Society Publication, Committee on Chemical Safety.

13.16 *"Carcinogens – Working with Carcinogens"*, Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

Table 1 - Equipment & Supplies

Supplies	Vendor	Catalog #
Separatory Funnel, 2L	Fisher	K6360412000
Teflon Stopper	Fisher	K8505400034
Erlenmeyer filter flask, 250mL	Fisher	10-090-B
Erlenmeyer filter flask, 500mL	Fisher	10-091-C
Filter funnels, 75mm	Fisher	10-346B
Graduated cylinder, 1000mL Class A	Fisher	08-548G
Rapid-Vap flask, 1 mL	Fisher	16-315-74
Whatman #41 Filter paper	Fisher	09-8500
pH Indicator paper [0-6]	Fisher	M95863
pH Indicator paper [5-10]	Fisher	M95883
pH Indicator paper [7.5-14]	Fisher	M95873
Serological Pipettes, disposable, 1mL	Fisher	13-678-25B
Serological Pipettes, disposable, 2mL	Fisher	13-678-25C
Pipette bulb	Fisher	13-681-102B
Vial/Caps/Septa Clear Vials, 2mL	Kimble/Fisher	60886A-1232
Clear vials, 40mL	QEC	1112-40mL
Glass Wool	Supelco	2-0410
Teflon Squirt Bottle, 500mL	Fisher	03-409-12E
Eppendorf autopipettor, 100-1000µL	Fisher/Brinkmann	05-1402-50 / 22-47-030-2
Pasteur pipettes, disposable, 5.75 in.	Fisher	13-678-6A
3D Floor Shaker		VS550424
Rapid Vap N2	Labconco	79100
Centrifuges	International Equipment Co.	
Separatory funnel racks		

Table 2 - Reagents and Standards

Supplies	Vendor	Catalog #
Methylene Chloride, 4L	Fisher	D151-4
Hexane, 4L	Fisher	H303-4
Acetonitrile, 4L	Fisher	A996-4
Hydrochloric Acid, 2.5L	Fisher	A508-212
Sodium Hydroxide, 3Kg	Fisher	S318-3
Sodium Sulfate, 2.5Kg	Fisher	S415-212
Methanol, 4L	Fisher	A454-4
Acetone, 4L	Fisher	A928-4

Table 3 pH Adjustments

Method	Initial Extraction pH	Second Extraction pH	Exchange Solvent required for analysis		Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8081/8082	5 – 9	None	Hexane		10.0	10.0
8140	6 – 8	None	Hexane		10.0	1.0
8141	received	None	Hexane		10.0	1.0
8015M	< 2	none	None		-	1.0
8310	Received	None	Acetonitrile		-	1.0
8270C**	< 2	> 11	None		1.0	1.0

* The cleanup procedures for Method 8081/8082 may vary according to the list of analytes. The following cleanups may be performed:

Analyte	Cleanup
Pesticide	Method 3620 Florisil Cleanup
PCB	Method 3665A Sulfuric Acid Cleanup

** The specificity of GC/MS may make cleanup of the extracts necessary. Refer to the supervisor or laboratory director for guidance on the cleanup procedures available if required.

Table 4 - Surrogates and Spikes

Surrogate/Spike	Description	Vol.	Application
BNAs by 8270C / 625			
Surrogate #1	Acid	1 mL	All
Surrogate #2	Base/Neutral	1 mL	All
Matrix Spike #1	Full List Spiking Solution	5 mL	LCS/LCSD & MS/MSD
Acid Extractables by 8270C / 625			
Surrogate #1	Acid Surrogate	1 mL	All
Matrix Spike #1	Acid Spiking Solution	1 mL	LCS/LCSD & MS/MSD
Base Neutrals by 8270C / 625			
Surrogate #2	Base/Neutral	1 mL	All
Matrix Spike #1	Full List Spiking Solution	5 mL	LCS/LCSD & MS/MSD
Phthalates by 8270C / 625			
Surrogate #2	Base/Neutral	1 mL	All
Matrix Spike #1	PHTH Spiking Solution	1 mL	LCS/LCSD & MS/MSD
PAHs by 8270C / 625			
Surrogate #2	Base/Neutral	1 mL	All
Matrix Spike #2	8310 Spiking Solution	2 mL	LCS/LCSD & MS/MSD
PEST & TCLP PEST by 8081A			
Surrogate #1	Pesticide Surrogate	1 mL	All
Matrix Spike #1	Pesticide MS	1 mL	LCS/LCSD & MS/MSD
PCB & TCLP PCB by 8082			
Surrogate #1	Pesticide Surrogate	1 mL	All
Matrix Spike	PCB MS	1 mL	LCS/LCSD & MS/MSD
DRO & TCLP TPH by 8015			
Surrogate #1	OTP Surrogate	1 mL	All
Matrix Spike	DRO Spike	1 mL	LCS/LCSD& MS/MSD
TCLP BNA by 8270C			
Surrogate #1	Acid Surrogate	1 mL	All
Surrogate #2	Base Surrogate	1 mL	All
Matrix Spike #1	Full List Spiking Solution	5 mL	LCS/LCSD & MS/MSD
PAH by 8310			
Surrogate #1	8310 Surrogate	1 mL	All
Matrix Spike #1	8310 Spiking Solution	1 mL	LCS/LCSD & MS/MSD

Ultrasonic Extraction by Method 3550B

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

1.1 Method 3550B is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of < 20mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The medium/high concentration method (individual organic components of > 20mg/kg) is much simpler and therefore faster.

2.0 Summary of Method

2.1 Low concentration method - A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing mixture. This is solvent extracted three times using ultrasonic extraction. The extract is concentrated and then analyzed using an appropriate analytical method.

2.2 Medium/high concentration method - A 2 g sample is mixed with anhydrous sodium sulfate. This mixture is solvent extracted once using ultrasonic extraction. The extract is separated from the sample by vacuum filtration, centrifugation or filtration. The extract is ready for cleanup and/or analysis following concentration.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts of interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and solvents may be necessary.

3.1.1 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.1.2 Glassware contamination can result in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem Chromic acid that is not completely rinsed will cause similar problems with analyte degradation and should be carefully rinsed to avoid this problem.

3 2 Refer to Organic Laboratory Glassware Cleaning Procedure SOP

4.0 Equipment and Apparatus

4 1 Refer to Table 1 for a listing.

5.0 Reagents and Standards

5 1 Policy.

5.1 1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents/solvents/standards must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

5.1 2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Program (SVQAP). This program is detailed in the Quality Assurance Program Plan Section 6.3. Refer to Reagent and Standard Solutions Validation. SOP

5.2 Solutions/Standards-See *SW846 Method 3500* for surrogate and spike information.

5.3 Sodium sulfate (granular, anhydrous) is used with filter paper to help prevent water from getting through the filter and to dry the sample to a free flowing, sandy mixture. It is placed in the oven at 170°C in its original container and left overnight to dry. It is then moved to a dessicator until needed The sodium

sulfate is pre-rinsed with the appropriate extraction solvent prior to use. Sixty grams of sodium sulfate will be used as the clean matrix for all method blanks extracted using 3550B.

5.3.1 Refer to Table 2 for a listing of reagents and standards.

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

6.1.1 Refer to *Chapter 2 of SW-846* and Sample Login Procedures SOP for guidance concerning containers, preservation and holding times.

6.2 Storage of Samples Prior to Extractions at 4±2 °C.

6.3 Storage of Extracts Prior to Analysis at 4 ±2°C.

6.4 Holding Times

6.4.1 Holding Time for extraction is defined as the number of days from ***Sample Collection*** (e.g. Sample Date) to extraction.

6.4.2 Holding Time for analysis is defined as the number of days from ***Sample Extraction*** in the laboratory to date injected/analyzed by the instrument.

7.0 Procedure

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Gummy, fibrous or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling of these difficult matrices.

7.1.3 Determination of Dry Weight: When samples are to be reported as dry weight an aliquot of the original sample is taken and appropriate methodology is applied for the determination of dry weight. This factor is applied to the subsequent analytical result. This procedure is performed in the inorganic laboratory

7.2 Extraction method for samples expected to contain low concentrations of organics and pesticides (< 20mg/kg):

7.2.1 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately a 30.0g sample into a 250mL beaker. Record the weigh to the nearest 0.1g. Add 60g of anhydrous sodium sulfate and mix using a tongue blade. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing. Add surrogate standards to all samples, QC samples, and blanks (see Method 3500 for details on the surrogate standard solution and the matrix spike solution). For the sample LCS and MS/MSD in each analytical batch selected for spiking, add the matrix spiking standard. See Table 3. Immediately add 60mL of the extraction solvent

7.2.2 Place the bottom surface of the tip of the disrupter horn about 1/2 in. below the surface of the solvent, but above the sediment layer.

7.2.3 Extract ultrasonically for 2 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50%. of time). Do not use microtip probe.

7.2.4 Decant and filter extracts through Whatman 41 filter containing pre-rinsed sodium sulfate or using vacuum filtration or centrifuge, if necessary.

7.2.5 Repeat the extraction two more times with two additional 60 mL portions of solvent Decant off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample into the funnel and rinse with extraction solvent.

7.2.6 At the time that samples are ready for concentration, pour extract into the Rapid Vap N_2 flasks. The evaporator should be set as follows:

Soil Samples	
BNA	
Time	approx. 40 minutes
Temp	50 °C
Vortex	50
	lc
Pest & PCB's (Water and Soil)	
Time	approx 40 minutes
Temp.	50 °C
Vortex	50
Final volume	10mL exchanged to Hexane
BNA Water Samples	
Time	approx. 60 minutes
Temp	50 °C
Vortex	50
Final volume	1mL Methylene chloride
For DRO Concentrations (Water and Soil)	
Time	approx 40 minutes
Temp	50°C
Vortex	50
Final volume	1mL Methylene chloride

CAUTION: When the volume of solvent is reduced below 1mL, semi-volatile analytes may be lost.

7.2.7 The Rapid-Vap N_2 Evaporation System should be already on at a set temperature of 50°C and a Vortex speed of 50%.

7.2.8 Place the sample tubes in the Rapid-Vap at a volume not to exceed 250mL due to possible contamination. Lower the lid to start nitrogen flow and vortexing motion.

Note: It is critical that the extract not be allowed to evaporate to dryness. If this occurs, re-extraction of the sample is required.

7.2.9 Set the timer and continue to concentrate the samples until a final volume that is acceptable for the specific method is obtained. This volume is usually 1mL. If the sample concentrates below the 1mL mark let the Rapid-Vap flask cool, then add the preferred solvent to the sample and bring it to volume.

7.2.10 If you need to exchange the solvent, concentrate the extract down to 2mL, add at least 30mL of preferred solvent and reconcentrate down to the desired final volume. Remove from the Rapid-Vap until you are ready to transfer to 2mL or 40mL vials.

7.2.11 Transfer the extract from the sample tube to the vial. If the final volume is 0.01 to 4mL, use a serological pipette and pipette bulb to draw the solvent to the desired final volume for the appropriate test.

7.2.12 If the final volume is 5mL or above pour the extract into a graduated cylinder and bring it up to the volume which is required for the test

7.2.13 The extract obtained may now be analyzed for analyte content using a variety of organic techniques. If analysis of the extract or any step in the extraction procedure will not be performed immediately, cover the flask with aluminum foil and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a Teflon-lined screw cap or crimp top, and labeled appropriately.

7.3 Extraction method for samples expected to contain high concentrations of organics (> 20 mg/kg):

7.3.1 Transfer approximately 2g (record weight to the nearest 0.1g) of sample to a 250mL beaker.

7.3.2 Add 2 g of anhydrous sodium sulfate to the sample in the beaker and mix well.

7.3.3 Surrogate standards are added to all samples, spikes, and blanks (see *SW846 Method 3500* for details on the surrogate standard solution and on the matrix spike solution).

7.3.4 Immediately add 60mL of Methylene chloride-Acetone mixture. Disrupt the sample with the 1/8 in. tapered microtip ultrasonic probe for 2 minutes at output control setting 5 and with mode switch on pulse and percent duty cycle at 50%. Extraction solvent always used is methylene chloride-acetone mixture during the concentration exchange step.

7.3.5 Filter the extract through a Whatman 41 filter.

7.3.6 The extract is now ready for concentration. Proceed with 7.2.7 for concentration.

8.0 Quality Control/Quality Assurance

8.1 Refer to Chapter One of SW 846 for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

8.2 Any reagent blanks or matrix spike samples should be subject to exactly the same analytical procedures as those used on actual samples.

8.3 Corrective Action - Corrective Action is the process by which problems within the laboratory are identified, proper personnel are notified, the problem solved or justified, correction implemented and the Corrective Action documented.

8.4 Sonicator Tuning Procedure

The sonicator(s) are to be tuned at a frequency of a minimum of once quarterly using the following procedures:

8.4.1 Ensure that the probe or microtip is not immersed in the liquid and that it does not come in contact with anything. If a cup horn or flow through cell is used, make sure that it does not contain any liquid.

8.4.2 Set PULSER to OFF position.

8.4.3 Set OUTPUT CONTROL to "10" (to "5" when using a microtip).

8.4.4 Set POWER SWITCH to ON. The switch will illuminate.

8.4.5 Momentarily depress TUNE SWITCH and rotate the tuner clockwise or counterclockwise until a minimum (not maximum) reading (usually less than 20) is obtained on the POWER MONITOR. If a minimum reading cannot be obtained, the probe, cup horn, tip, microtip, extender, or accessory is loose or out of resonance, or the power supply or converter require servicing. A loose probe will usually generate a loud piercing sound.

8.4.6 Set OUTPUT CONTROL to "4".

8.4.7 Set POWER SWITCH to OFF.

8.4.8 With a dual output 600 watt Ultrasonic Processor, if two converters are going to be used simultaneously, connect at this time the second converter cable to the top connector.

Caution: The power supply should be tuned after the probe has reached operating temperature. When working with low or high temperature liquids, immerse the probe in the liquid for a few minutes, withdraw the probe out of the liquid, then, tune the power supply. When using the optional cup horn or continuous flow cell, remove all the water from the cup horn, and liquid from the continuous flow cell, before tuning the power supply.

When using a microtip or extender, never allow the tip to vibrate in air for more than 15 seconds and do not set the OUTPUT CONTROL above "5". Disregarding these instructions will cause the microtip or extender to fracture.

Note: The probe is tuned to vibrate at a specific frequency. If the resonant frequency of the probe has changed, due to cavitation erosion or fracturing, minimum reading will not be

obtained. If minimum reading cannot be obtained, check the unit without the probe. If proper tuning is obtained without the probe, the probe should be changed.

9.0 Training and Training Validation

Employee training on documented procedures may be found in the Employee Training SOP. Demonstration of the employee's training in the specific procedures involved in this method may be found in the Training Documents Log This documentation includes all in-house and outside training received and include items such as proficiency testing and information on performance testing results. A Demonstration of Capability is on file for each analyst performing the test.

10.0 Data Validation

Refer to the Data Reduction and Review SOP.

11.0 Health and Safety

Refer to the Chemical Hygiene Plan and Laboratory Safety Plan SOPs.

12.0 Waste Disposal and Pollution Management

Refer to the Waste Management Plan SOP for waste disposal procedures.

13.0 References

13.1 LMP's Definitions, Acronyms, Symbols and Abbreviations Policy
13.2 Solid Waste Manual, SW846 Update III, December 1996.
13.3 U.S Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements EM 200-1-3, 1 Feb 01.
13.4 EPA, Methods for Chemical Analysis of Water and Wastes, EPA –600/4-79-020, March 1983.
13.5 NELAC, Quality Systems, Revision 15, May 25, 2001.
13.6 NELAC, Program Policy and Structure, Revision 13, June 29, 2000.
13.7 40 CFR Part 136 Appendix A.
13.8 EPA Guidance for Preparing Standard Operating Procedures (SOPs), EPA QA/G-6, EPA/240/B-01/004, March 2001
13.9 USEPA 2185 – Good Automated Laboratory Practices
13.10 USEPA 600/4-79-020, Methods for Chemical Analysis of Water and Wastes, March 1983.
13.11 OSHA Laboratory Standard, 29 CFR 1910 1450.
13.12 OSHA Compliance Guide, Kirk H. Ray, 8th Edition.
13.13 *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986
13.14 Laboratory Safety in Practice. A Comprehensive Compliance Program and Safety Manual.
13.15 *"Safety in Academic Chemistry Laboratories"*, American Chemical Society Publication, Committee on Chemical Safety.

Table 1 - Equipment & Supplies

Supplies	Vendor	Catalog #
Erlenmeyer filter flask, 250mL	Fisher	10-090-B
Erlenmeyer filter flask, 500mL	Fisher	10-091-C
Beakers, 250mL	Fisher	02-555-20A
Filter funnels, 75mm	Fisher	10-346B
Rapid-Vap flask, 1 mL	Fisher	16-315-74
Whatman #41 Filter paper	Fisher	09-8500
Serological Pipettes, disposable, 1mL	Fisher	13-678-25B
Serological Pipettes, disposable, 2mL	Fisher	13-678-25C
Pipette bulb	Fisher	13-681-102B
Vial/Caps/Septa Clear Vials, 2mL	Kimble/Fisher	60886A-1232
Clear vials, 40mL	QEC	1112-40mL
Teflon Squirt Bottle, 500mL	Fisher	03-409-12E
Pasteur pipettes, disposable, 5.75in.	Fisher	13-678-6A
Eppendorf autopipettor, 100-1000µL	Fisher/Brinkmann	05-1402-50 / 22-47-030-2
Wooden tongue depressors	Fisher	01-346
Balance - Top loading		
Rapid Vap N2	Labconco	Model 79100
Centrifuges	International Equipment Co.	
Ultrasonic disrupter		
Ultrasonic tips/horns		
Sonabox	Ultrasonics, Inc.	Model 432B or equivalent

Table 2 - Reagents and Standards

Supplies	Vendor	Catalog #
Methylene Chloride, Pesticide quality or equivalent		
Hexane:Acetone, Pesticide quality or equivalent		
Acetone, GC Resolv	Fisher	A928-4
Methylene-Acetone 1:1, Pesticide quality or equivalent		
Hexane	Fisher	303-4
Acetonitrile	Fisher	A996-4

Table 3 - Specific Extraction Conditions For Various Determinative Methods

.Method	Initial extraction pH	Extraction Solvent	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup as Necessary (mL)	Final extract volume for analysis (mL)
8081A	Neutral pH	Methylene Chloride-Acetone 1:1	Hexane	Hexane	10.0	10.0
8082	Neutral pH	Methylene Chloride-Acetone 1:1	Hexane	Hexane	10.0	10.0
8310	Neutral pH	Methylene Chloride	Acetonitrile	None	NA	1.0
8270	Neutral pH	Methylene Chloride-Acetone 1:1	None	None	NA	1.0

(a) The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

Mercury in Liquid Waste, Automated Cold-Vapor Technique

By SW-846 Method 7470A

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

Methods 7470A is a cold-vapor atomic absorption procedure for determining the concentration of mercury in aqueous wastes and ground water samples.

2.0 Summary of Method

2.1 The cold-vapor technique is based on the absorption of radiation at 253.7nm by mercury vapor. The mercury is reduced to the elemental state and separated from solution by a gas/liquid separator. The mercury vapor passes through a cell positioned in the light path of a mercury lamp. Absorbed radiation is measured as a function of total mercury.

3.0 Interferences and Potential Problems

Certain metals like Copper have been known to interfere with the analysis of Mercury.
Likewise, anions such as chloride must be eliminated with the use of potassium permanganate, since it absorbs radiation of 253nm.

4.0 Equipment and Apparatus

4.1 CETAC M-6000 Mercury Analyzer with autosampler
4.2 Water bath
4.3 Eppendorf variable pipette
4.4 Eppendorf tips
4.5 16 X 100 culture tubes
4.6 Digitubes
4.7 Viton Pump windings
4.8 Filtermates
4.9 Nist-Traceable thermometer
4.10 25 mL graduated cylinder
4.11 Transfer pipettes (disposable)
4.12 Black/black pump windings
4.13 Yellow/yellow pump windings

Refer to Table 1.

5.0 Reagents and Standards

All reagents and solutions are prepared, identified and documented. Refer to Reagent and Standard Solutions Validation SOP. All stock solutions shall be valid for 6 months and intermediates or working standards will be held for 1 month unless otherwise specified by the method or superseded by USACE Shell Document EM 200-1-3. Store these solutions in appropriate containers Follow the preparation, storage and expiration protocols as described in the aforementioned SOP on Standard and Reagent Preparation and Traceability or as indicated below.

5.1 ASTM Type II water
5.2 Concentrated Hydrochloric Acid, Trace Metal Grade
5.3 Concentrated Nitric Acid, Trace Metal Grade
5.4 Concentrated Sulfuric Acid, Trace Metal Grade
5.5 Stannous Chloride: Add 50 grams of $SnCl_2$ to 500 mL Type II Water and 37.0 ml concentrated HCl.
5.6 Sodium chloride-hydroxylamine sulfate solution: Add 120 grams NaCl and 120 grams hydroxylamine sulfate into 1000 mL of deionized water.
5.7 Potassium Permanganate solution: Add 50 grams of $KMnO_4$ into 1000 mL deionized water
5.8 Potassium Persulfate solution: Add 50 grams of K_2SO_8 into 1000 mL deionized water.
5.9 Ultra-Pure Zero-Grade Argon Gas UN1006
5.10 Mercury Stock.
5.11 Mercury Stock (second source)

6.0 Sample Preservation and Containers

6.1 The Holding Time for this analysis from the time of collection of the sample is 28 days.
6.2 Samples should be collected in plastic bottles and samples preserved to pH of less than 2 with concentrated

nitric acid.

7.0 Procedure – Sample Preparation

7.1 Prepare standards (refer to Table 6). These will be taken through the entire preparation procedure. Standards are prepared daily. Record SRN#'s in Log.

7.2 All data is recorded in the Metals Digestion Logbook (refer to Table 2). The following information is required to begin the procedure:

- ❑ Date and Time
- ❑ Initials of Technician
- ❑ Next consecutive number of Logbook (Digestion Batch)

7.3 Organize the LIMS generated worksheets (refer to Table 3) into batches of up to 20 samples. Record the LMP Sample ID of each selected sample in the Metals Digestion Logbook.

7.4 To establish which sample is to be used as the Matrix Spike, the following criteria is used:

- ❑ Adequate volume of sample available
- ❑ Sample must not be a Field QC (e.g., Trip Blank, Equipment Blank)
- ❑ Client specific request (e.g. sample or project)
- ❑ Select last sample of digestion batch.

7.5 Once the spike sample is selected, record the MS/MSD sample ID in the Metals Digestion Logbook.

7.6 Assign each sample in the digestion log a unique identifier (e.g. #1 through #20 for the first batch, #1A through #20A for the second batch…). Transcribe the unique identifier to the corresponding digestion tube (i.e. digitube) using a black Sharpie pen

7.7 Invert samples 3 to 4 times to ensure settled solids are consistently distributed.

7.8 Immediately transfer 20 mL of well-mixed sample directly into the digitube.

7.9 For the sample selected for the MS/MSD, triplicate aliquots are prepared.

7.10 Prepare two (2) aliquots of 20 mL deionized water to use for Method Blank and LCS

7.11 Transfer 20 mL from each calibration standard volumetric into a digitube. Check the Calibration logbook to be sure the Eppendorf has been calibrated for the day (refer to Table 4).

7.12 Spike the LCS, MS and MSD with 0.1mL of Mercury spiking solution (refer to Table 5) using the Eppendorf variable pipette. Record the SRN number of the spiking solutions used in the Mercury Digestion Logbook.

7.13 Add 0.5mL of HNO_3 and mix. Record RRN#'s in Log.

7.14 Add 1.0mL of H_2SO_4 and mix. Record RRN#'s in Log.

Note: When adding acid, look for any reaction in the samples that may require dilutions. If reaction is noted, ask supervisor. Make appropriate dilutions.

7.15 Add 3 mL of potassium permanganate solution to each digestion vessel and mix. Add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Note in Digestion Log any additional permanganate needed. Record SRN#'s in Log

7.16 Add 0.8 mL of potassium persulfate to each vial and mix. Do this twice. Record SRN#'s in Log

7.17 Cap each tube and place rack in water bath. Record temperature of bath in Digestion Log.

7.18 Digest in two autoclave for 20 minutes.

7.19 Remove racks from autoclave and allow cooling to room temperature

7.20 Remove caps and add 1.2 mL of sodium chloride hydroxylamine sulfate. Use a disposable transfer pipette to mix. Record SRN#'s in Log

7.21 Filter, if necessary, with Filtermate.

8.0 Procedure – Sample Analysis

8.1 Power up system Allow 30 minutes to warm up.

- ❑ Mercury lamp
- ❑ A/S
- ❑ Gas (set to deliver 100 psi)
- ❑ Computer / Monitor
- ❑ Set and clamp pump windings on peristaltic pump

8.2 Before turning peristaltic pump on, be sure to remove outlet line form gas liquid separator.

8.3 Turn pump on and make any pressure adjustments necessary to achieve steady flows.

8.4 Enter method in software.
Note: CETAC M-6000 is operated and controlled using the proprietary software created by CETAC Technologies, Inc. Analyst will be trained on software capabilities and procedures.

8.5 Analyze the 10µg/L standard and make any gas flow adjustments necessary to achieve an adequate intensity level (e.g., if 10µg/L standard is reading 30,000 intensity units, the gas flow might need to be reduced to achieve approximately 40,000 to 50,000 intensity units).

8.6 Using the profile of the 10µg/L standard set the time profile lockdown and the baseline correction points.

8.7 Transfer calibration digestates into the appropriate A/S tubes.

8.8 Calibrate the instrument using 5 standards and a blank. (correlation coefficient = ≥ 0.995).

8.9 Build autosampler sequence using the Digestion Log. Sequence must begin with an Initial Calibration Blank and Initial Calibration Verification. Transfer LMP Sample ID's into autosampler sequence, making sure to add a Continuing Calibration Blank and Continuing Calibration Verification every 10 samples.

8.10 Transfer digestates into a 16 X 100mm culture tube in the autosampler rack.

8.11 Analyze samples

9.0 Quality Control

9.1 The instrument will automatically analyze all samples in quadruplicate. The resulting %RSD should be ≤ 10%.

9.2 The minimum correlation coefficient required is 0.995 for the initial calibration.

9.3 An Initial Calibration Blank is analyzed at the start of each analytical run. Result must be less than the established quantitative limit

9.4 An Initial Calibration Verification Check is analyzed at the start of every run. The concentration for this check standard is 5.0µg/L. The acceptance criterion is that it must be ± 10 %.

9.5 A reagent blank is taken through the entire procedure, one for every extraction batch or 20th sample, whichever is more frequent. The result must be less than 0 10µg/L.

9 6 A Laboratory Control Sample is taken through the entire procedure; one for every extraction batch or 20th sample, whichever is more frequent. The percent recovery must fall between 80-120%

9.7 Matrix spike and spike duplicate samples are analyzed every analytical batch (20 samples) or daily, whichever is more frequent. The percent recovery should fall between 80-120% and the RPD must be less than 20%.

9 8 A Continuing Calibration Check standard is analyzed every 10 samples and at the end, and recorded on the run log. Results must be ± 20%.

9.9 An Continuing Calibration Blank is analyzed every 10 samples and at the end and the result should be less than the established quantitative limit.

9.10 An Ending Calibration Check is analyzed at the end of the analytical sequence and the result should be within 20%

10.0 Calculations

All calculations are handled by CETAC instrument software and have been validated.
From the calibration curve generated, the slope and y-intercept are generated and recorded. It should be noted that because we are dealing with a linear model, the calculated correlation coefficient should be greater than 0.995. These will be the variables used in the calculation of sample concentration The equation used is:

$$\text{Hg, µg/L} = \quad X = \frac{(Y - B)}{A}$$

Where:
X = concentration of the sample, µg/L
Y = average response of the instrument for the sample
B = y-intercept
A = slope of the curve

11.0 Data Validation

Data validation is performed per Data Reduction and Review SOP

11.1 The analyst completes sequence Checklists for each analytical sequence. The analyst must complete the

checklist and ensure that all method Quality Assurance requirements have been met.

11.2 Calibration (ICAL) - Calibration criteria must be met prior to analysis of samples. No sample analysis may begin until calibration criteria have been validated and verified.

11.3 Initial calibration verification (ICV) is analyzed at the beginning of the analytical sequence. This standard is made using a second source stock standard. Results must be within ±10% of the expected value.

11.4 Continuing Calibration Verification (CCV) - Reported sample results for any analyte must be bracketed by CCV standards that are within ± 20% of the expected value for that analyte. In addition, the RPD for the duplicate injections must be less or equal to 20%. Re-analysis is required for those analytes outside the CCV evaluation criteria.

11.5 Continuing Calibration Blank (CCB) - CCBs are analyzed after every 10 samples and at the end of the analytical sequence. The CCB must be less than the MQL for each reported analyte. Re-analysis is required for those reported analytes outside the CCB evaluation criteria.

11.6 Reported results must be within the established calibration range. Analytes above this range must be diluted and re-analyzed.

11.7 A method blank must be less than the method quantitation limit (MQL) (for USCOE samples, less than 0.10 µg/L) If the blank is not less than the MQL, sample should be re-analyzed to verify failure. If sample is verified to be out of control, re-digestion and analyses of entire batch is required.

11.8 The LCS sample must fall within ± 20% of the expected value. If failure occurs, the entire batch will be considered out of control, re-digestion and analyses of entire batch is required.

11.9 Results for the MS, MSD samples should be < 20% Recovery and < 20% RPD. If failure occurs and a sample is < 2 µg/L, a post digestion spike (PDS) will be necessary on the spiked sample. Results of the PDS should be ± 15% recovery of the expected value. If sample is > 2 µg/L and MS,MSD fail, a dilution test (DT) will be required Results of a 1:5 dilution and the original sample result should be within 10% difference.

11.10 If DT or PDS were used and a failure occurs, the Method of Standard Additions (MSA) will be necessary. Re-digestion and re-analysis may be used if further verification is required.

11.11 Once the sequence has been reviewed, the analyst will complete any applicable QC Forms needed to summarize any Quality Control Samples analyzed. Refer to Table 7.

- Method Blank Summary
- Laboratory Control Sample(s)
- Matrix Spike/Matrix Spike Duplicate
- Dilution Test Summary
- Post Digestion Spike Summary (PDS)
- Method of Standard Additions Summary (MSA)

11.12 The analyst is required to complete, review, sign and date the work sheets prior to submission (Level I review).

11.13 The Section Supervisor (or designate) will then review the work sheet to ensure completeness and accuracy (Level II review). The Section Supervisor is ultimately responsible for the quality of the Level II review. The Metals Laboratory Supervisor is responsible for ensuring that all worksheets, reagent logs digestion logs and standard logs and maintenance logs are completed and up to date.

12.0 Training and Training Validation

12.1 Employee training on documented procedures may be found in the Employee Training SOP.

12.2 Demonstration of the employee's training in the specific procedures involved in this method may be found in the Training Documents Log This documentation includes all in-house and outside training received and include items such as proficiency testing and information on performance testing results. A Demonstration of Capability is on file for each analyst performing the test.

13.0 Health and Safety

Refer to the Chemical Hygiene Plan and Laboratory Safety Plan SOPs

14.0 Waste Disposal and Pollution Management

Refer to the Waste Management Plan SOP for waste disposal procedures.

15.0 References

- LMP's Definitions, Acronyms, Symbols and Abbreviations Policy
- Solid Waste Manual, SW846 Update III, December 1996.
- U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements Version 1.0 2 NOV 98.
- EPA, Methods for Chemical Analysis of Water and Wastes, EPA –600/4-79-020, March 1983.
- NELAC, Quality Systems, Revision 15, May 25, 2001.
- NELAC, Program Policy and Structure, Revision 13, June 29, 2000
- 40 CFR Part 136 Appendix A.
- EPA Guidance for Preparing Standard Operating Procedures (SOPs), EPA QA/G-6, EPA/240/B-01/004, March 2001
- USEPA 2185 – Good Automated Laboratory Practices
- USEPA 600/4-79-020, Methods for Chemical Analysis of Water and Wastes, March 1983.
- OSHA Laboratory Standard, 29 CFR 1910.1450.
- OSHA Compliance Guide, Kirk H. Ray, 8th Edition.
- *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.
- Laboratory Safety in Practice. A Comprehensive Compliance Program and Safety Manual.
- *"Safety in Academic Chemistry Laboratories"*, American Chemical Society Publication, Committee on Chemical Safety.
- *"Carcinogens – Working with Carcinogens"*, Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

Tables

Table 1 - Equipment & Supplies

Supplies	Vendor	Catalog #
CETAC M-6000	CETAC	NA
Water bath	Chefs Supply	NA
Eppendorf Variable Pipette	Fisher	85-402-50
Eppendorf tips	Fisher	2235090-1
Digitubes	SCP Science	010-500-263
16 X 100 Culture tubes	SCP Science	130-012-006
Viton pump windings	CETAC	S5704
Black/black pump windings	CETAC	S5705-B
Yellow/yellow pump windings	CETAC	S5705-A
Filtermates	Environmental Express	SC0401
25 mL Graduated cylinder	Fisher	20024
Nist-Traceable Thermometer	Fisher	14-983-19A
Conc. HNO_3 (Trace metal grade)	Fisher	A509-212
Conc. H_2SO_4 (Trace metal grade)	Fisher	A510-212
Conc. HCl (Trace metal grade)	Fisher	A508-212
Stannous Chloride	Fisher	T142-500
Sodium Chloride	Fisher	S271-3
Hydroxylamine Sulfate	Fisher	H331-500
Potassium Permanganate	Fisher	7068/UN1490
Potassium Persulfate	Fisher	P282-500
Ultra Pure Zer-Grade Argon	Nexair	UN1006
1000 mg/L Mercury Standard	CPI	4400-1000331
1000 mg/L Mercury Standard	Environmental Express	100033-1

Table 4

Office of Quality Assurance
Variable Auto-Pipettor Daily Calibration Log
Ref: USACE Shell Document EM 200-1-3 1 Feb 01 Section I.9.1.3
Balance:

Pipettor Serial No.:	Lab:	uL Setting	Reading 1 (grams)	Reading 2 (grams)	Reading 3 (grams)	Ave Weight (grams)	Within 3%
Calibration Date and Initials							

Reading taken at ambient temperature with specific density of water at 0.9982 g/ml.
Acceptance Criteria for 100-ul setting: 0.0968 - 0.1028 grams
Acceptance Criteria for 1000-ul setting: 0.9683 - 1.0281 grams

1) Record Date and Initials
2) Set pipette to 1000 µL setting
3) Tare out scale capable of ± 0.0001
4) Weight first aliquot
5) Record weight
6) Repeat steps 3-5 twice more
7) Calculate the average
8) Record average
9) Average must fall within the acceptance criteria listed above.

Note: For more information, refer to Calibration of Support Equipment SOP.

Table 5

Working Standard Dilution Schedule

Instrument Calibration	
Dilution 1	1:100 of 1000mg/L Hg stock standard
Dilution 2	1:100 of Dilution 1 standard
Initial Calibration Verification	
Second Source	1:100 of Second Source 1000mg/L Hg Stock Standard
Spiking Solution	1:1000 Dilution of 1000mg/L Hg Stock Standard

Standard is preserved with a volume of HNO_3 to achieve 1% v/v. Record the SRN# in the SRN Log.

Table 6
Components of 5-point Curve

The following components are generated from various Hg stock solutions at different volumes. Consult the Standard Reagent Log for details. The curve set will be documented using one unique identifier for the total set with will include the following components.

Components of the 5-point curve set include:

ICAL 1: 0.20µg/L Hg Standard: 2mL of 0.10mg/L Hg Standard +1mL HNO_3 into 100 mL deionized water
ICAL 2, 1.00µg/L Hg Standard: 1mL of 0.10mg/L Hg Standard +1mL HNO_3 into 100 mL deionized water
ICAL 3, 2.00µg/L Hg Standard: 2mL of 0.10mg/L Hg Standard +1mL HNO_3 into 100 mL deionized water
ICAL 4, 5.00µg/L Hg Standard: 5mL of 0.10mg/L Hg Standard +1mL HNO_3 into 100 mL deionized water
ICAL 5, 10.0µg/L Hg Standard:10mL of 0.10mg/L Hg Standard +1mL HNO_3 into 100 mL deionized water

A new curve is generated daily or whenever new reagents are usd to prepare the curve. This new curve will be documented in the Standard Reagent Logbook.

A separate ICV is generated using an independent source. Consult the Standard Reagent Log and this SOP for details on preparation.

8772096

Mercury in Solid Waste, Automated Cold-Vapor Technique

By SW-846 Method 7471A

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

Method 7471A is a cold-vapor atomic absorption procedure for determining the concentration of mercury in solid or semi-solid wastes.

2.0 Summary of Method

Samples are prepared according to the procedure described in this method.
The cold-vapor technique is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and separated from solution in a gas\liquid separator. The mercury vapor passes through a cell positioned in the light path of a mercury lamp. Absorbed radiation is measured as a function of total mercury.

3.0 Interferences and Potential Problems

Certain metals like Copper have been known to interfere with the analysis of mercury.
Likewise, anions such as chloride must be eliminated with the use of potassium permanganate, since it absorbs radiation of 253 nm.

4.0 Equipment and Apparatus

4.1 Culture tubes that are 20mm X 150mm

4.2 CETAC M-6000A Mercury Analyzer with long 22-cm absorbance cells (reference and sample).

4.3 Water bath set at 90 - 95°C

4.4 Nafion Dryer Kit

4.5 Digestion Tubes with screw caps (Environmental Express Cat. SC 499).

5.0 Reagents and Standards

All reagents and solutions are prepared, identified and documented following SOP QASRPT02.DOC Standard and Reagent Preparation and Traceability. All stock solutions shall be valid for 6 months and intermediates or working standards will be held for 1 month unless otherwise specified by the method or superseded by USACE Shell Document EM 200-1-3. Store these solutions in appropriate containers. Follow the prepartion, storage and expiration protocols as described in the aforementioned SOP on Standard and Reagent Preparation and Traceability.

5.1 ASTM Type II water

5.2 Concentrated Nitric Acid, HNO_3 – Trace Metal Grade

5.3 Concentrated Hydrochloric Acid, HCl – Trace Metal Grade

5.4 Stannous Chloride, $SnCl_2$: Dissolve 50 grams $SNCl_2$ in 500 mL Type II water and 37.0 mL concentrated HCl.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 120 grams NaCl and 120 grams hydroxylamine sulfate in 1000 mL Type II water

5.6 Potassium Permanganate solution, $KMnO_4$: Dissolve 50 grams $KMnO_4$ in 1000 mL Type II water.

5.7 Aqua Regia: Prepare immediately before use by adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

5.8 Ultra-Pure Zero-grade Argon Gas , UN 1006

5.9 Mercury Stock Solution, 1000 mg/L, Environmental Express (Initial Calibration Source) Observe the expiration date as indicated by the manufacturer If no information is provided stock solutions will be held for 6 months.

5.10 ICAL Intermediate 1, 10 mg/L: Place 5.00 mL Mercury Stock Solution and 10.0 mL nitric acid into a total volume of 500 mL of deionized water. This solution is valid for 1 month.

5.11 ICAL Intermediate 2, 1.0 mg/L: Place 10.0 mL of ICAL Intermediate 1 and 1.0 mL of nitric acid into a total volume of 100 mL deionized water. This solution is valid for 1 month.

5.12 ICAL 1, .004 mg/L: Pipet 1 mL of ICAL Intermediate 2 and 2 mL of nitric acid into 250 ml deionized water. Prepare this standard daily.

5 13 ICAL 2, 0.02 mg/L: Pipet 2 mL of ICAL Intermediate 2 and 1 mL of nitric acid into 100 mL deionized water. Prepare this standard daily.

5.14 ICAL 3, 0.04 mg/L: Pipet 4 mL of ICAL Intermediate 2 and 1 mL of nitric acid into 100 mL deionized water. Prepare this standard daily.

5 15 ICAl 4, 0.10 mg/L: Pipet 10 mL of ICAL Intermediate 2 and 1 mL of nitric acid into 100 mL deionized water. Prepare this standard daily.

5.16 ICAL 5, 0.20 mg/L: Pipet 20 mL of ICAL Intermediate 2 and 1 mL of nitric acid into 100 mL deionized water. Prepare this standard daily.

5.17 Initial Calibration Verification Stock Standard, 1000 mg/L, CPI. Independent Source. Observe the expiration date as indicated by the manufacturer. If no information is provided stock solutions will be held for 6 months.

5.18 ICV Intermediate 1S, 10 mg/L: Pipet 5 mL of ICV Stock Solution and 10 mL of nitric acid into a final volume of 500mL deionized water. Intermediate solutions are valid for one month.

5 19 ICV Intermediate 2S, 1 mg/L. Pipet 10 mL of ICV 1S and 1 mL of nitric acid into a final volume of 100 mL deionized water. Intermediate soluitons are valid for one month.

6.0 Sample Preservation and Containers

6 1 The Holding Time for this analysis from the time of collection of the sample is 28 days.

6.2 Samples should be collected in glass wide mouth jars and samples and stored at 4oC.

7.0 Procedure- Sample Preparation and Analysis

7 1 Weigh 0.6000 g +/- 10% soil sub-sample into a digestion tube Record this weight on the extraction logsheet.

7.2 Add 1 mL of Type II water to samples and 0.1 mL of spiking solution to the Laboratory Control and MS/MSD and swirl to mix. Then add 0.4 mL HNO_3, and 1.00 mL H2SO4 to all samples. Swirl to mix

7.3 Add 1 mL saturated potassium permanganate solution.

7.4 Heat in a water bath at 90- 95° C for 30 minutes. The water bath is monitored by a working thermometer which as has been calibrated against an NIST-Traceable thermometer. This calibration is conducted minimally once a year. Autoclave for 20 min. at 120oC then cool.

7.5 Add 1.4 mL sodium chloride-hydroxylamine sulfate to reduce the excess permanganate, filter if necessary. Then add 19 ml deionized water.

7.6 Samples and associated QC samples are now ready for analysis

7.7 For the dedicated instrument, follow manufacturers instructions for setting up and optimizing instrument. See Daily Checklist

7.8 Calibrate instrument using a series of five standards and a calibration blank. The standards consist at concentrations of 0 2, 1.0, 2.0, 5.0 and 10.0 ug/L. The calibration curve is run daily.

7.9 Samples are then automatically introduced into the instrument by the peristatic pump, where they are mixed with stannous chloride, reducing the mercury to a vapor.

7.10 The mercury vapor is then swept by argon gas delivering it to the absorbance cell, where radiation of 253.7 um is absorbed. The resulting electrical analog signal is converted to digital (A/D) which is then processed by the software to yield a binary digital number, which is plotted against previously obtained absorbance versus concentration values from known standards to give the amount of analyte present.

8.0 Quality Control

8.1 The instrument will automatically analyze all samples in quadruplicate. The resulting % RSD should be $\leq$ 10%.

8.2 The minimum correlation coefficient of 0.995 is required.

8.3 An Initial Calibration Blank is analyzed at the start of every analytical run. Result must be less than the established detection limit of 0.02 mg/Kg.

8.4 An Initial Calibration Verification Check is analyzed at the start of every run. The concentration for this check standard is 5.0 ug/L. The acceptance criteria is that it must be +/- 10 %.

8.5 A Reagent Blank is taken through the entire procedure every 20 samples or daily, whichever is more frequent. Result must be less than the established detection limit of 0.02 mg/Kg.

8.6 A Laboratory Control Sample is taken through the entire procedure, every 20 samples or daily, whichever is more frequent. The percent recovery should fall between 80-120%.

8.7 Matrix spike and spike duplicate samples are analyzed every analytical batch (20 samples) or daily, whichever is more frequent. The percent recovery should fall between 80-120% and the RPD must be less than or equal to 20%.

8.8 A Continuing Calibration Verification Standard, (CCV) and a Continuing Calibration Blank, CCB, analyzed every 10 samples and recorded on the run log. Results must be +/- 20% for the CCV and below the detection limit for CCB.

8.9 An Ending Calibration Blank is analyzed and the result should be less than the established detection limit.

8.10 An Ending Calibration Check is analyzed at the end of the analytical sequence and the result should be within +/- 20%.

9.0 Calculations

All calculations are handled by CETAC instrument software and have been validated.
From the calibration curve generated, the slope and y-intercept is generated and recorded. These will be the variables used in the calculation of sample concentration. The equation used is:

$$\text{Hg, ug/L} = \qquad X = \frac{(Y - B)}{A}$$

Where:
X = Concentration of the sample, ug/L
Y = Average response of the instrument for the sample
B = y-intercept
A = slope of the curve

10.0 Data Validation

Data validation is performed per procedures detailed in the Quality Manual.

10.1 Sequence Checklists are completed for each analytical sequence by the analyst Example forms are provided in Appendix B. The analyst must complete the check list and ensure that all method Quality Assurance requirements have been met :

Calibration (ICAL) - Calibration criteria must be met (Section 8.1- 8.4) prior to analysis of samples. No sample analysis may begin until calibration criteria have been validated and verified.
Continuing Calibration Verification (CCV) - CCVs are analyzed after every 10 samples and at the end of the analytical sequence. Reported sample results for any analyte must be bracketed by CCV standards that are within +/-20% of the expected value for that analyte. In addition, the RSD for the duplicate injections must be less than or equal to 20% Re-analysis is required for those analytes outside the CCV evaluation criteria.
Continuing Calibration Blank (CCB) - CCBs are analyzed after every 10 samples and at the end of the analytical sequence. The CCB must be less than the MDL for each reported analyte. Re-analysis is required for those reported analytes outside the CCB evaluation criteria
Reported results must be within the established calibration range. Analytes above this range must be diluted and re-analyzed.

10.2 Once the sequence has been reviewed, the analyst will complete any applicable QC Forms needed to summarize any Quality Control Samples analyzed.

Method Blank Summary
Laboratory Control Sample(s)
Matrix Spike/Matrix Spike Duplicate
Dilution Test Summary
Post Digestion Spike Summary (PDS)
Method of Standard Additions Summary (MSA)

10.3 The analyst is required to complete, review, sign and date the work sheets prior to submission (Level I review)

10.4 The Section Supervisor (or designate) will then review the work sheet to ensure completeness and accuracy (Level II review). The Section Supervisor is ultimately responsible for the quality of the Level II review.

The Metals Laboratory Supervisor is responsible for ensuring that all work sheets, reagent logs, standard logs and maintenance logs are completed and up to date.

11.0 Waste Management

Refer to LMP's SOP Waste Management Plan.

12.0 Health and Safety

Refer to LMP, Inc.'s SOP Chemical Hygiene and Laboratory Safety Plans.

13.0 Training & Training Validation

Consult the Employee Training SOP.

14.0 References

14.1 "Carcinogens – Working with Carcinogens", Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No 77-206, August 1977

14.2 "OSHA Safety and Health Standards, General Industry", 29 CFR 1910.

14.3 "Proposed OSHA Safety and Health Standards, Laboratories", Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.

14.4 "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety.

14.5 Solid Waste Manual, SW846 Update III, December 1996

14.6 Code of Federal Regulations 40 CFR Part 136.

14.7 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements, Appendix H.

14.8 EPA, Chemical Analysis of Water and Waste, EPA 600\4-79-020.

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ICP Analysis of Metals

By SW-846 Method 6010B

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

Method 6010B, Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) is used to determine the concentrations of select metals in digestates of liquid and solid matrices. Refer to Table 1B.

2.0 Summary of Method

2.1 Prior to analysis, samples are digested using the appropriate sample preparation techniques. The following methods are applicable: 3005A, 3050B, 3051.

2.2 This method describes the simultaneous multi-elemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the resulting intensities of the lines are monitored by photomultiplier tubes.

3.0 Interferences and Potential Problems

3.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element at the analytical or background measurement wavelengths, (2) unresolved overlap of molecular band spectra, (3) stray light from the line emission of high concentration elements.

3.2 Element-specific interference is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 50-1000 mg/L of the interfering element. Table 4 lists the interelement correction factors. All interelement correction factors must be updated at least once every 12 months and whenever there is a significant instrument modification.

3.3 Stray light from the line emission of high concentration elements are indicated on the instrument print out by either "S - Saturation - peak intensity overflow" or "k - calculation error due to problem calculating IEC from S". These samples must be diluted to ensure that this stray light does not effect sample results.

3.4 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample Another problem that can occur with high dissolved solids is salt build-up at the tip of the nebulizer, which effects aerosol flow rate and causes instrument drift. The problem can be controlled by diluting those samples known to be high in dissolved solids. Changing or cleaning the nebulizer and removing salt buildup at the tip of the center tube (torch) can be used as an additional measure to control salt buildup. A mass flow controller is also used to compensate for variations in flow and improve instrument performance.

4.0 Equipment and Apparatus

4.1 Thermo Jarrel Ash Enviro I – Trace Analyzer with 27 Elements

4.2 Thermo Jarrel Ash AS-300 position autosampler

4.3 Volumetric glassware, Class A

5.0 Reagents and Standards

All reagents and solutions are prepared, identified and documented. Refer to Reagent and Standard Solutions Validation SOP.

5.1 Deionized water - ASTM Type II

5.2 Concentrated nitric acid (Trace Metal Grade), A509-212

5.3 Concentrated hydrochloric acid (Trace Metal Grade), A508-212

5.4 Stock calibration standards are purchased from Accustandard and CPI. Table 1 summarizes the current solutions used.

5.5 Mixed calibration standard solutions (ICAL) - Prepare mixed calibration standards by combining appropriate volumes of the stock solutions in volumetric flasks Refer to Table 1 for the calibration standard dilution schedule. All calibration standards are matrix matched with the appropriate acid and diluted with deionized water. The mixed standards have been verified by the manufacturer to ensure that the elements are stable and compatible. The mixed standards are transferred to previously unused polyethylene or

polypropylene bottles for storage. Calibration standards are prepared at a minimum of every six months and monitored daily for signs of degradation.

5.6 Calibration Verification Standards (CCV) - Prepare mixed calibration standards by combining appropriate volumes of stock standards from an independent source from the stock initial calibration standards. See Table 1A for the calibration verification standard dilution schedule. All CCVs are matrix matched with the appropriate acid and diluted with deionized water. The mixed standards have been verified by the manufactured to ensure that the elements are stable and compatible The mixed standards are transferred to previously unused polyethylene or polypropylene bottles for storage

5.7 Low Level Check (LLC) - Prepare the mixed low-level calibration standard from an independent source from stock initial calibration standards. See Table 2 for the standard dilution schedule. This solution will have a 6-month expiration date.

5.8 Interference Check Standard (ICS) - Prepare the mixed interference check standards from an independent source from the stock initial calibration standards. See Table 2 for the standard dilution schedule.

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements. Refer to *Chapter 2 of SW-846* for guidance concerning containers, preservation and holding times.. Also refer to LMP's Sample Login Procedures SOP and the appropriate digestion method SOP for holding times, preservatives and containers.

7.0 Procedure

7.1 Instrument / Method Set-up

7.1.1 The Linear Dynamic Range (LDR) is verified for each analyte on an annual basis. The concentration is analyzed at the manufacturers recommended upper analytical range. The analyte concentration analyzed must be within 10% of the expected concentration The linear dynamic range is used to determine the appropriate concentration for the high calibration standard The concentration for the high calibration standard must be below the established linear dynamic range. Refer to Table 3 for LDR summary.

7.1.2 The Linear Calibration Range (LCR) is defined as the high calibration standard in the initial calibration procedure. Any sample concentration greater than the LCR MUST be diluted and reanalyzed. See Table 3 for LCR summary.

7.1.3 Method detection limits (MDLs) are established by analyte for each method of digestion. The MDLs are performed annually.

7.1.4 All Interelement Spectral Correction Factors (IECs) are determined on an annual basis or whenever there are significant instrument modifications Element-specific interference is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 50-1000 mg/L of the interference element. Table 4 lists the analytes and the IECs (resulting correction factors).

7.1.5 Three exposures are performed for all standards, samples and quality control samples. The mean of each set of exposures is used for quantitation or calibration. The exposure time is specified in the method and must be verified by monitoring the time required for the sample or standard to reach the mixing chamber and equilibrate in the torch. This is checked whenever pump winding, autosampler tubing, or the nebulizer is changed or cleaned. RSD criteria for Initial Calibration and Continuing Calibration are defined in Section 10.1.

7 2 Analytical Procedures

7 2 1 Set up the instrument with the proper operating parameters The instrument must be allowed to become thermally stable before beginning with the profile and calibration procedures. This requires a minimum of 30 minutes prior to continuing.

7.2 2 The ICP must be profiled at the beginning of each analytical shift. This procedure consists of nebulizing a 5mg/L arsenic standard and observing both the resulting intensity and spectral shift. This information is printed each analytical shift. The spectrum shifter is adjusted if necessary, so that the resulting analytical line is within +/- 0.1 units.

7.2.3 An Initial Calibration (ICAL) must be performed at the beginning of each analytical shift. The initial calibration consists of a high-level standard and a calibration blank The concentration of the high-level standard is less than the upper limit of the linear dynamic range of the instrument and represents the upper

reporting limit for each analyte (Refer to Table 3 for Linear Calibration Range). Three exposures are performed for all initial calibration standards, and the RSD of these multiple exposures is printed each analytical shift and monitored to verify the introduction system's reproducibility. The maximum RSDs for the high-level calibration standards is 5%. The dilution schedule for the initial calibration solutions are detailed in Table 1.

7.2.4 After the initial calibration is complete, an Initial Calibration Blank (ICB) is analyzed. Each analyte concentration in the ICB must be less than the reported MDL. If this criteria is not met, corrective action must be taken. A check table is created in the TJA method software to assist in the evaluation of the ICB by setting acceptance criteria for each element of interest.

7.2.5 Before beginning sample analysis, the initial calibration standards must be verified against the initial calibration curve. This verification consists of reanalyzing the calibration standards as if they were samples (read-back). Concentration values obtained must not deviate from the actual values by more than 5%. If this criteria is not met, the instrument must be recalibrated and the initial calibration standards reanalyzed. A check table is created in the TJA method software to assist in the evaluation of the initial calibration standards by setting low and high acceptance criteria for each element of interest.
After the blank (ICB) standard has met read-back criteria the Initial Calibration Verification (ICV) standards are analyzed. The ICVs are calibration standards from an independent source. For all analytes of interest, the ICVs represent a mid-level calibration standard, and must be within 10% of the actual value. A check table is created in the TJA method software to assist in the evaluation of the initial calibration verification standards by setting low and high acceptance criteria for each element of interest. The dilution schedule for the ICV solutions is detailed in Table 1A.

7.2.6 For USCOE sample: With the two-point calibration (high-level standard and a calibration blank) additional verification of a low-level standard must be performed. The Low Level Check (LLC) is analyzed to ensure accuracy of concentration at the method-reporting limit. The acceptance criteria for the LLC is 20% of the actual concentration. If the 20% criteria cannot be met, then the LLC may be re-analyzed for those analytes that failed. If these analytes fail after the re-analysis, then the system is considered out of control and corrective action must be taken prior to recalibration. A check table is created in the TJA method software to assist in the evaluation of the LLC by setting low and high acceptance criteria for each element of interest. The dilution schedule for the LLC is detailed in Table 1B.

7.2.7 In order to adequately test the interelement correction factors established in the instrument / method setup, an Interference Check Standard (ICS) must be analyzed. The ICS consists of two check standards, which must be analyzed at the beginning and the end of the analytical sequence. The ICS-A contains only the interferents while the Interference Check Standard AB (ICS-AB) contains both the interferents and all other analytes of interest. The criterion for the ICS standard is listed below:

> The ICSAB solution contains all analytes of interest. The concentration of these analytes must be within 20% of the expected value.

All analytes that fail ICS-A evaluation must be reanalyzed under a new initial calibration/ICS-A evaluation.
The dilution schedule for the ICSA and ICSAB are detailed in Table 1B.

7.2.8 The initial calibration curve must be verified throughout the course of the analytical sequence. This is accomplished by the analysis of both Continuing Calibration Verification Standards (CCVs) and Continuing Calibration Blanks (CCBs) The CCVs and CCBs are analyzed after every 10 samples or quality control samples and at the end of the analytical sequence. The results of the CCV must agree within 10% of the expected value and the RSD for the three replicate exposures must be <5%. If not, terminate the analysis for those analytes outside acceptance criteria, correct the problem and reanalyze the previous ten samples. The results of the CCB must be less than the MDL for each analyte of interest. All reported sample results must be bracketed by acceptable CCBs and CCVs.

7.3 Digestion Procedures

7.3.1 Digestion procedures are detailed in the applicable preparation procedures.

7.3.2 At a minimum, each digestion batch will contain the following QC samples: (Refer to Section 8.0 for evaluation/acceptance criteria.)

a. Method Blank
b. Laboratory Control Sample(s)

c. Matrix Spike/Matrix Spike Duplicate
d. Post Digestion Spike

8.0 Quality Control/Quality Assurance/Corrective Action

8.1 A Method/Reagent Blank (MB) is taken through the entire procedure each analytical batch or daily, whichever is more frequent. The MB must be processed at the same time and in the same manner as the samples, in order to assess potential contamination from the laboratory reagents, equipment, or environment. The concentration of all target analytes shall be below one-half of the reporting limit (MRL) for each target analyte, or less than 5 percent of the regulatory limit associated with that analyte, or less than 5 percent of the sample result for the same analyte, whichever is greater for the MB to be acceptable.
Note: Matrix specific method detection limits are listed and determined according to specific digestion procedures.

8.2 Laboratory control samples (LCS) are taken through the entire procedure each analytical batch or daily, whichever is more frequent. The LCS is spiked with the all Target Analytes and must be processed with each batch of samples in order to verify that the analytical and preparatory procedures are in control in an interference-free matrix. The default control limits for the LCS are 80-120% for aqueous or solid matrix. If recoveries for the LCS are out of control, corrective action must be taken. The source of the problem must be investigated and the effect on the samples must be evaluated. For example, if an analyte in the LCS has a recovery above the upper acceptance limit, but the same analyte is not detected in any of the environmental samples in the batch or is detected at less than 5% of the action level, additional corrective measures may not be necessary. For all other situations, reanalyze the LCS extract to verify the out-of-control condition. If the LCS remains out of control, evaluate the batch using the following.

8 2.1 LMP, Inc has adopted the following policy regarding LCS evaluation:

a. LCS recovery is high for an analyte not identified in any samples associated with the LCS. The data will be considered valid as the high recovery indicates that detection limits were not affected. The analyte(s) recovery should be monitored daily for a trend that might indicate the need for corrective action No re-extraction/re-analysis required.

b. LCS recovery is high for an analyte identified in samples associated with the LCS. The LCS and sample(s) should be re-digested/re-analyzed for the failing analyte only. If the LCS and sample(s) cannot be re-digested (e.g., holding time expired, no additional sample available...) then the final result must be flagged as "J - Estimated Value" and a Case Narrative provided detailing the exact recovery of the LCS.

c. LCS recovery is low for an analyte not identified in samples associated with the LCS. The LCS and sample(s) should be re-digested/re-analyzed for the failing analyte only. If the LCS and sample(s) cannot be re-digested (e.g., holding time expired, no additional sample available then the final result must be flagged as "J - Estimated Value" and a Case Narrative provided detailing the exact recovery of the LCS

d. LCS recovery is low for an analyte identified in samples associated with the LCS. The LCS and sample(s) should be re-digested/re-analyzed for the failing analyte only. If the LCS and sample(s) cannot be re-digested (e.g., holding time expired, no additional sample available...) then the final result must be flagged as "J - Estimated Value". A Case Narrative must be provided detailing the exact recovery of the LCS and that the reported value for the flagged analyte represents a minimum value.

8 3 Laboratory Control Sample Duplicates - LCSD

8.3.1 LCSDs are digested under the following circumstances:

8.3.1.1 Not enough sample available to perform both MS/MSD

8.3.1.2 Only sample available for MS/MSD is a Field Blank or Equipment Rinsate. No MS/MSD is to be extracted on these type samples.

8 3.1.3 Required by the project Sampling and Analytical Plan

8.3.2 RPD limits for LCS/LCSD should not exceed 20%

8 3.3 If duplicate precision for the LCS is not in control, corrective action must be taken. However, if RPDs are outside of control limits, the batch need not be rejected (as long as the recoveries are acceptable).

8.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD) are taken through the entire procedure each analytical batch or daily, whichever is more frequent. The MS/MSD is spiked with all Target Analytes and is processed with each batch of samples to assess the performance of the preparatory / analytical methods in a particular matrix. The default control limits for the MS/MSD are 75-125%.

8.5 Every batch of samples must contain at least one Post-Digestion Spike (PDS) in order to evaluate the performance of the analytical method in a particular matrix for USCOE samples only. By spiking the digestate with a known amount of standard, the PDS allows an assessment of the analytical method without influence of the preparatory procedure. If at all possible the sample chosen for the MS/MSD should be also undergo the PDS. Target analytes spiked in the PDS should be the same concentration as the MS. This assists in evaluating matrix interference that could occur during either the digestion or analytical procedure. The default control limits for the PDS is 75-125%.

8.6 Evaluation of Matrix Interference: The MS and PDS must have a spike concentration at least twice as great as the unspiked sample concentration for the following evaluation to be considered valid. Corrective action must be taken in the following scenarios:

8.6.1 The MS/MSD recoveries fail but the PDS recovery passes. This condition would not require re-digestion/re-analysis as the MS/MSD act as verification of the low recoveries due to matrix interference.

8.6.2 The MS/MSD recoveries pass and the PDS recovery fails. This condition would require re-analysis of the PDS to confirm or disprove laboratory error during PDS spiking. The MS recovery pass, MSD recovery fails and the PDS passes. Evaluate %RPD. If RPD is within limits then the passing MS validates the MSD and the PDS is equivalent to a single point MSA. If the RPD is out, then a problem may have occurred with the MSD during digestion. Re-digest/re-analyze the MSD for verification.

8.6.3 If the MS/MSD recoveries do not meet minimum recovery limits but the PDS passes, redigestion and reanalysis is not required if the metal has historically exhibited low MS recoveries. Antimony in soil is an example of chronic low recoveries exhibited in the MS.

8.6.4 MS/MSD recoveries fail, PDS fails Analyze by MSA.

8.6.5 If the MS recoveries are due to a high level of Target Analyte(s) present in the sample relative to the spike amount, then corrective action may not be necessary. High levels of Target Analyte(s) may indicate the need for a Dilution Test.

8.6.6 RPD limits for the MS/MSD should not exceed 20%.

8.6.7 If duplicate precision for the MS/MSD is not in control, corrective action must be taken. However, if RPDs are outside of control limits, the batch need not be rejected (as long as the recoveries are acceptable). If the RPD criteria is not met, reanalyze the MSD and calculate the %RSD for the set of three analyses (MS/MSD and reanalysis of MSD). If the %RSD for the set of three analyses is greater than 15%, matrix interference is confirmed.

8.7 When both the MS and PDS indicate matrix interference, the Method of Standard Additions (MSA) is required before qualifying the results as effected by matrix interference.

8.8 A Serial Dilution or Dilution Test (DT) is performed for an analyte to evaluate matrix interference if the analyte concentration is the original undiluted sample is at least 25 times the detection limit. The DT is a 1:5 dilution, where the results of the undiluted and diluted sample should have a RPD of <10%. If the RPD is >10%, matrix effects are suspected and MSA is to be performed.

9.0 Calculations

All calculations are handled by TJA ThermoSpec software and have been validated. The purpose of the emission spectrometer is to measure the concentration of elements of interest in a sample. The first step in this process is the measuring of emission intensity produced when a sample containing these elements are aspirated into the plasma. The emissions intensities must then be converted into reports of concentration. In order to do this, the relationship between emission intensity and concentration must be first determined using standard materials whose concentrations are accurately known. This is termed standardization. Hence, standard materials are used to determine the coefficients of the equations, which related the emission intensity to concentration.

Because of the spectral characteristics of the plasma, relating intensity ratio to concentration is often very simple. Plasma emission spectroscopy is capable of producing calibration curves, which are linear over several magnitudes. Since optical emission spectroscopy is a comparative technique, standards are used to establish the relationship between concentration and intensity rations. As indicated, standardization is a procedure for

calculating this relationship. This laboratory uses the two-point standardization option employing, a blank and a high standard for each element of interest. Generally, the equation below illustrates how the intensity ratios obtained for these standards relate to the concentration of the standards:

$$C = M (IR) + B$$

Where: C = concentration
IR = intensity Ratio obtained for each standard
M = slope of the line, which relates the concentration of the standards with the intensity ratios
B = intercept of the line which relates the concentration of the standards with the intensity ratios

The use of a two-point standardization allows for a linear fit. The standardization procedure is used for updating intensity ratio now to the intensity at the time the instrument was first calibrated. The output of the Standardization Algorithm is Standardized Intensity Ratio, SIR. The relation is

$$SIR = M^* IR + B$$

Where: SIR = standardized intensity ratio
M = slope of the lines which relates the current intensity ratios to the originally measured intensity ratios
IR = intensity ratio measured now
B = intercept of the lines, which relates the current intensity ratios to the originally measured intensity ratios

During the two-standardization process, IR, the Intensity Ratio measured NOW and SIR, the Intensity Ratio measured INITIALLY, are obtained for both the blank and each high standard. These are used to construct two simultaneous equations, which solve for M and B. A Standardization Report is generated which indicate M (slope) and B (y-intercept) for each evaluated element. Also included in this report are the wavelength in nanometers, indication of which initial calibration standard is used for each element and the date and time of the standardization. The instrument will plot signal versus concentration. Note that signal represents an intensity ratios. Once these coefficients are evaluated, the equations can be used to convert IRs for unknown samples, QC check standards or blanks to SIRs. From this process, a calibration table is constructed and comparisons are made between the unknowns, QC samples and blanks to the constructed linear plots

Because the data from this instrument is collected in concentration mode, mg/L, the instrument is standardized first as described above then defaults to the option:

$$Slope = Conc (SIR) / IR$$

In the Standardization Report, only Standard Deviation and RSD are calculated from three repetitive readings. Refer to *EPA SW846 Method 8000B* for calculation description

Likewise, in the Standardization Report, an average response is calculated from the three repetitive readings using the equation, mean RF as indicated above. To be valid, the %RSD calculated must be less than 5%.

As noted, a blank and high standard are used in the standardization and calculation of unknowns, blank and QC samples. For this purpose, a high standard is utilized from 4 Initial Calibration Standards who collectively contain all the elements of interest.

From the several steps indicated above, three readings are taken from each sample for each elements of interest and an average calculated in the concentration mode, mg/L.

10.0 Data Validation

Data validation is performed per Data Reduction and Review SOP.

10.1 Sequence Checklists are completed for each analytical sequence by the analyst. An example forms are provided in Appendix B. The analyst must complete the check list and ensure that all method Quality Assurance requirements have been met·

- Initial Calibration (ICAL) - ICAL criteria must be met prior to analysis of samples. No sample analysis may begin until ICAL criteria have been validated and verified. This includes the analysis of the ICB, Read-Back, ICV, LLC and ICS verifications.
- Continuing Calibration Verification (CCV) - CCVs are analyzed after every 10 samples and at the end of the analytical sequence. Reported sample results for any analyte must be bracketed by CCV standards that are within +/-10% of the expected value for that analyte. In addition, the RSD for the three- (3) replicate exposures must be 5% or less. Re-analysis is required for those reported analytes outside the CCV evaluation criteria.
- Continuing Calibration Blank (CCB) - CCBs are analyzed after every 10 samples and at the end of the analytical sequence. The CCB must be less than the MDL for each reported analyte. Re-analysis is required for those reported analytes outside the CCB evaluation criteria.
- Reported results must be within the established calibration range. Analytes above this range must be diluted and re-analyzed.

10.2 Once the sequence has been reviewed, the analyst will complete any applicable QC Forms needed to summarize any Quality Control Samples analyzed.

- Method Blank Summary
- Laboratory Control Sample(s)
- Matrix Spike/Matrix Spike Duplicate
- Dilution Test Summary
- Post Digestion Spike Summary (PDS)
- Method of Standard Additions Summary (MSA)

10.3 The analyst is required to complete, review, sign and date the work sheets prior to submission (Level I review).

10.4 The Section Supervisor (or designate) will then review the work sheet to ensure completeness and accuracy (Level II review). The Section Supervisor is ultimately responsible for the quality of the Level II review.

10.5 The Metals Laboratory Supervisor is responsible for ensuring that all work sheets, reagent logs, standard logs and maintenance logs are completed and up to date.

11.0 Training and Training Validation

Employee training on documented procedures may be found in the Employee Training SOP. Demonstration of the employee's training in the specific procedures involved in this method may be found in the Training Documents Log This documentation includes all in-house and outside training received and include items such as proficiency testing and information on performance testing results. A Demonstration of Capability is on file for each analyst performing the test.

12.0 Data Validation

Refer to the Data Reduction and Review SOP

13.0 Health and Safety

Refer to the Chemical Hygiene Plan and Laboratory Safety Plan SOPs.

14.0 Waste Disposal and Pollution Management

Refer to the Waste Management Plan SOP for waste disposal procedures.

15.0 References

- LMP's Definitions, Acronyms, Symbols and Abbreviations Policy
- Solid Waste Manual, SW846 Update III, December 1996 and Method 6010B Rev. 2 Dec. 1996.
- U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical EM 200-1-3 1 Feb 01.
- EPA, Methods for Chemical Analysis of Water and Wastes, EPA –600/4-79-020, March 1983.
- NELAC, Quality Systems, Revision 15, May 25, 2001.
- NELAC, Program Policy and Structure, Revision 13, June 29, 2000

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- 40 CFR Part 136 Appendix A.
- EPA Guidance for Preparing Standard Operating Procedures (SOPs), EPA QA/G-6, EPA/240/B-01/004, March 2001
- USEPA 2185 – Good Automated Laboratory Practices
- USEPA 600/4-79-020, Methods for Chemical Analysis of Water and Wastes, March 1983.
- OSHA Laboratory Standard, 29 CFR 1910.1450.
- OSHA Compliance Guide, Kirk H. Ray, 8th Edition.
- *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.
- Laboratory Safety in Practice. A Comprehensive Compliance Program and Safety Manual.
- *"Safety in Academic Chemistry Laboratories"*, American Chemical Society Publication, Committee on Chemical Safety.
- *"Carcinogens – Working with Carcinogens"*, Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

Tables

Table 1
Standards

C1				
Component	**Catalog#**	**Conc. (mg/L)**	**Dilution**	**Final Conc. (mg/L)**
Aluminum	ICP-09N-5-10X	10,000	1:100	100
Calcium	ICP-01N-5-10X	10,000	1:100	100
Iron	ICP-27N-5-10X	10,000	1:100	100
Magnesium	ICP-32N-5-10x	10,000	1:100	100
C2				
Silver	ICP-53N-1	1000	1:1000	1
Arsenic	ICP-03N-1	1000	1:1000	1
Barium	ICP-04N-1	1000	1:100	10
Beryllium	ICP-05N-1	1000	1:1000	1
Cadmium	ICP-08N-1	1000	1:1000	1
Cobalt	ICP-14N-1	1000	1:100	10
Chromium	ICP-13N-1	1000	1:100	10
Copper	ICP-15N-1	1000	1:100	10
Manganese	ICP-33N-1	1000	1:100	10
Nickel	ICP-37N-1	1000	1 100	10
Lead	ICP-297N-1	1000	1:1000	1
Selenium	ICP-51N-1	1000	1:1000	1
Thallium	ICP-60N-1	1000	1:1000	1
Vanadium	ICP-67N-1	1000	1.100	10
Zinc	ICP-70N-1	1000	1:100	10
C3				
Boron	ICP-07W	1000	1.100	10
Antimony	ICP-02N-1	1000	1:1000	1
Tin	ICP-63N-1	1000	1:100	10
Strontium	ICP-55N-1	1000	1:1000	1
Titanium	ICP-64W-1	1000	1:100	10
Molybdenum	ICP-35N-1	1000	1:100	10
C4				
Potassium	ICP-43N-1	1000	1:100	10
Sodium	ICP-54N-1-10X	10,000	1:1000	10

Table 1A
ICV, CCV Spiking Solutions

Spiking Solution 1			
Catalog#	**Dilution**	**Component**	**Conc. (mg/L)**
440-132894	1:100	Silver	50
		Arsenic	50
		Boron	500
		Barium	500
		Beryllium	50
		Cadmium	50
		Cobalt	500
		Chromium	500
		Copper	500
		Potassium	500
		Manganese	500
		Molybdenum	500
		Sodium	500
		Nickel	500
		Lead	50
		Antimony	50
		Selenium	50
		Tin	500
		Strontium	50
		Titanium	500
		Thallium	50
		Vanadium	500
		Zinc	500
Spiking Solution 2			
Catalog#	**Dilution**	**Component**	**Conc. (mg/L)**
440-132894	1:100	Aluminum	5000
		Calcium	5000
		Iron	5000
		Magnesium	5000

Table 1B
ICP Standard Summary – ICSA/AB and LLC

Analyte	Catalog #	Vendor	Stock Concentration, mg/L
Ag	ICP-53N-1	AccuStandard	1000
Al	ICP-O1N-5-10X	AccuStandard	10000
As	ICP-O3N-1	AccuStandard	1000
B	ICP-O7W	AccuStandard	1000
Ba	ICP-O4N-1	AccuStandard	1000
Be	ICP-O5N-1	AccuStandard	1000
Ca	ICP-09N-5-10X	AccuStandard	10000
Cd	ICP-08N-1	AccuStandard	1000
Co	ICP-14N-1	AccuStandard	1000
Cr	ICP-13N-1	AccuStandard	1000
Cu	ICP-15N-1	AccuStandard	1000
Fe	ICPI-27N-5-10X	AccuStandard	10000
K	ICP-43N-1	AccuStandard	1000
Mg	ICP-32N-5-10X	AccuStandard	10000
Mn	ICP-33N-1	AccuStandard	1000
Mo	ICP-35N-1	AccuStandard	1000
Na	ICP-54N-1-10X	AccuStandard	10000
Ni	ICP-37N-1	AccuStandard	1000
Pb	ICP-29N-1	AccuStandard	1000
Sb	ICP-02N-1	AccuStandard	1000
Se	ICP-51N-1	AccuStandard	1000
Sn	ICP-63N-1	AccuStandard	1000
Sr	ICP-55N-1	AccuStandard	1000
Ti	ICP-64W-1	AccuStandard	1000
Tl	ICP-60N-1	AccuStandard	1000
V	ICP-67N-1	AccuStandard	1000
Zn	ICP-70N-1	AccuStandard	1000

Table 2
Low Level Verification / Interference Check Standards
Dilution Schedule

Analyte	Low Level Verification ug/L	Interference Check Standard mg/L
Aluminum	100	250(ICSA/ISCAB)
Antimony	8	.200 (ISCAB)
Arsenic	6	.200 (ICSAB)
Barium	20	.500 (ICSAB)
Beryllium	0.5	.200 (ICSAB)
Boron	50	.500 (ICSAB)
Cadmium	1	.200 (ICSAB)
Calcium	100	250 (ICSA/ICSAB)
Chromium	5	.200 (ICSAB)
Cobalt	10	.200 (ICSAB)
Copper	5	.200 (ISCAB)
Iron	100	100 (ICSA/ICSAB)
Lead	4	.200 (ICSAB)
Magnesium	100	250 (ICSA/ICSAB)
Manganese	10	.200 (ICSAB)
Molybdenum	5	.200 (ICSAB)
Nickel	10	.200 (ICSAB)
Potassium	100	5 (ICSAB)
Selenium	6	.200 (ICSAB)
Silver	5	.200 (ICSAB)
Sodium	200	5 (ICSAB)
Strontium	10	.200 (ICSAB)
Thallium	10	.200 (ICSAB)
Tin	50	.500 (ICSAB)
Titanium	10	.500 (ICSAB)
Vanadium	20	.500 (ICSAB)
Zinc	10	.200 (ICSAB)

Concentrations made from Standards in Table 1B.

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Table 3
Linear Dynamic Range / Linear Calibration Range Summary

Analyte	Linear Dynamic Range mg/L	Linear Calibration Range mg/L
Aluminum	500	100
Antimony	50	1
Arsenic	50	1
Barium	25	10
Beryllium	25	1
Boron	50	1
Cadmium	10	1
Calcium	500	100
Chromium	50	10
Cobalt	25	10
Copper	50	10
Iron	500	100
Lead	25	1
Magnesium	500	100
Manganese	50	10
Molybdenum	50	1
Nickel	25	10
Potassium	25	10
Selenium	50	1
Silver	25	1
Sodium	500	10
Strontium	10	1
Thallium	50	1
Tin	50	1
Titanium	10	1
Vanadium	100	10
Zinc	100	10

Table 4
Interelement Correction Factors

Aluminum	Fe: -0.000087	Mg: 0.000027	Ti: 0.002011
	V: -0.018878	Co: -0.016762	Mo: 0.023716
Antimony	Cr: 0.010375	Fe: 0.000024	Mo: 0.003846
	Ni: -0.004046	Ti: 0.001628	V: -0.004046
	Co: -0.001805	Sn: 0.001446	Pb: -0.000104
	Al: -0.000051	As: 0.000478	
Arsenic	Al: 0.005416	V: 0.005133	Co: 0.000695
	Cr: 0.001255	Cr: 0.001255	Ni: 0.000605
	Mg: -0.000047	Mn: -0.000843	Mo: 0.000763
	Fe: 0.000605		
Barium	Al: 0.000009	Ni: 0.00011	V: 0.00006
	Ti: 0.000051		
Beryllium	V: 0.000931	Ti: 0.000015	Cu: 0.000002
	Mo: -0.000049	Ni: 0.000005	
Boron	Fe: 0.000229	Mo: 0.039859	Ti: 0.006903
	Co: 0.002322	Sn: 0.004499	Al: -0.000002
Cadmium	Fe: 0.000203	Ti: 0.000184	Cr: -0.000108
	Mo: 0.000072	Al: 0.000008	Mg: -0.000003
	Co: 0.000039		
Calcium	Cr: 0.000611	Mo: 0.000556	V: 0.000581
	Ag: 0.000089	Mn: 0.000201	Al: 0.00005
	Ti: 0.000089		
Chromium	Fe: -0.000078	V: 0.001402	Mo: -0.003478
	Al: 0.000075	Cd: 0.000336	Ti: 0.000097
	Co: -0.000111	Mg: -0.000013	
Cobalt	Cd: 0.000611	Ti: 0.001463	Ni: 0.000301
	Ba: 0.000459		
Copper	Ti: 0.00078	Co: 0.000293	Fe: 0.000071
	Mo: 0.000579	V: 0.00004	Al: -0.000006
	Cr: 0.000058		
Iron	Tl: -0.000012	Be: -0.000106	Mn: -0.004944
	V: 0.000275	Al: 0.000138	Mo: 0.000399\
Lead	Co: -0.006642	Al: 0.000721	Fe: 0.000113
	Mo: -0.000492	Sb: -0.000745	Ti: 0.000686
	V: -0.000709	Mg: 0.000077	

Table 4 (continued)
Interelement Correction Factors

Magnesium	Ca: 0.000074	Fe: -0.000047	Tl: 0.000109
	Mn: -0.005083	Mo: -0.023101	Ti: -0.003818
	Be: -0.000391	Co: -0.000825	Cr: -0.000455
Manganese	Cu: -0.000324	Fe: -0.000179	Mo: -0.000193
	Al: 0.000007	V: -0.000069	Ti: 0.000019
Molybdenum	V: 0.000039	Ni: -0.000101	Fe: -0.000051
	Al: -0.000001		
Nickel	Mo: -0.002215	Co: 0.000255	Tl: 0.000843
	V: -0.000336	Mn: -0.000021	Sb: 0.000308
Potassium	Fe: -0.000528		
Selenium	Ca: -0.000311	Fe: -0.000326	Mg: -0.000106
	Co: 0.001476	Cd: -0.001976	Mn: -0.000522
	Sn: -0.000517		
Silver	Fe: -0.000329	Ti: -0.000381	V: -0.000219
	Mg: -0.000013	Ca: -0.000014	Mn: 0.000146
Sodium	Ti: 0.005408	Fe: -0.000013	Al: 0.000389
	Mo: 0.028573	Sn: 0.003359	Ca: 0.000084
	Cu: 0.000321	K: 0.000031	Mn: 0.000625
	V: 0.000463	Zn: 0.000121	
Strontium	Ca: 0.000021	Sn: 0.000004	Al: 0.000007
Thallium	Fe: 0.001918	Sn: -0.003967	V: 0.004244
	Ca: -0.000043	Co: 0.006637	Mn: 0.000876
	Mo: 0.000104	Ti: -0.409117	Na: -0.000101
	Cr: 0.000712	Pb: -0.000021	
Tin	Cr: 0.540233	Fe: -0.024306	Mo: 0.005683
	Ti: 0.009185	V: -0.073191	Mg: -0.000419
	Sr: -0.000152	Al: 0.000387	Mn: 0.001245
Titanium	Ca: -0.000296	Sb: 0.000015	Be: 0.000019
	V: 0.000031	Cr: 0.000341	Cu: 0.000062
	Mo: 0.000184	Al: 0.000002	Co: 0.000021
	Ni: -0.000019		
Vanadium	Cr: -0.003102	Cu: -0.000048	Mo: -0.002971
	Ti: 0.00021	Mn: -0.000149	
Zinc	Ba: 0.000005	Cu: 0.002437	Mn: 0.000121
	Fe: 0.000095	Ni: 0.003386	V: -0.008507
	Mg: -0.000004	Al: 0.000007	Ca: -0.000001

Standard Operating Procedure

For

Acid Digestion of Aqueous Samples for Total Recoverable or Dissolved Metals Analysis, EPA SW-846 3005A

Prepared by: S. Hanson_____ (signature)

Technical Director: M. Kauffman _____(signature)

1. Identification of Test Method

Acid Digestion of Aqueous Samples for Metals Analysis. The laboratory records and reports refer to this analysis as 3005A. This SOP based on metal preparation procedures of EPA SW-846 Method 3005A, Acid Digestion of surface water, ground water, and certain extracts.

2. Applicable Matrix or Matrices

This method is applicable to aqueous samples. Nitric acid digestates of surface water, ground water, and certain extracts are prepared using this method. Analytes other than those listed in the scope and application section may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest.

3. Detection Limits

The laboratory follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. Additionally, the laboratory determines the MDL whenever there is a significant change in equipment or substantive revision of the technical protocols for preparation and analysis of samples by this test method. The relative significance and substantiveness of any changes to equipment or protocols that may require redetermination of the MDLs shall be decided, and documented in QA files, by the QA Officer in conjunction with technical assistance from the laboratory Technical Director. All processing steps of the analytical method, including any routine preparation steps, are included in the determination of the MDL. The MDLs measured by the laboratory are on file for review in each determinative analytical procedure. All supporting documentation used in the determination of the laboratory MDLs is maintained in the laboratory QA files. These may include but are not limited to, laboratory prep batch worksheets, instrument printouts or Quantitation reports and MDL calculation spreadsheets.

The laboratory determined MDL must always be less than or equal to the reference method MDL. For those cases in which a regulatory compliance limit is in effect, the laboratory MDL must be less than one-third of the compliance limit.

MDL Check Samples are analyzed on a quarterly basis to verify the reported MDL when state or regulatory agencies require such.

4. Scope and Application

This method is applicable to the preparation of aqueous matrices for measurement of metals at various reporting levels depending upon the instrumentation used for analysis. This SOP is written for metals analysis using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Parameter List by Method and Matrix

Parameter	CAS
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Boron (B)	7440-42-8
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-98-7
Nickel (Ni)	7440-02-0
Phosphorus (P)	7723-14-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silica (SiO_2)	7631-86-9
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Thallium (Tl)	7440-28-0
Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6
Sulfur (S)	63705-05-5

The parameter list is extended to add metals commonly requested by clients for aqueous samples such as surface water, groundwater, and certain extracts.

5 Summary of Test Method

Various sample processing techniques must be considered and addressed appropriately for the parameters of interest including; total recoverable parameters using hot acid digestion techniques, and control of interferences. Sample processing includes the acid digestion of an accurately measured sample aliquot of a well mixed, homogeneous aqueous sample. The acid concentration and acids selected in the sample preparation step must be the same as the standards used for instrumentation calibration.

For the digestion of samples, a representative 50 mL sample is digested with nitric acid and hydrochloric acid. The resultant digestate is diluted to a final volume of 50 mL and either filtered or allowed to settle prior to the analytical procedure.

When analyzing for total dissolved metals, filter the sample at the time of collection, prior to acidification with nitric acid. If samples are not field filtered, the process is completed at the laboratory, prior to digestion. The date and time of sample filtering should be noted, along with the final results.

6. Definitions

The laboratory Quality Manual contains the definitions of standard terms used in this SOP. Additional terms are defined below.

Dissolved Metals—The sample is filtered through a 0.45 um filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards. If the un-acidified sample is filtered at the laboratory, the samples and all associated QC samples are acidified and are available for instrument analysis.

Total Recoverable Metals—The entire sample is acidified at the time of collection with nitric acid At the time of analysis the sample is heated with acid and substantially reduced in volume The digestate is either filtered or allowed to settle after being diluted to volume. The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid. The concentrations of analytes determined by this procedure are commonly known as total recoverable metals.

7. Interferences

Several types of interference effects may contribute to inaccuracies in the determination of trace elements. From the perspective of sample digestion, they can be summarized as follows:

Chemical Interferences are effects by a chemical or group of chemicals that cause the measurement of a target chemical or analyte to be incorrect.

Silver: Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, spiked sample matrices and spiked blanks or as a dissolved parameter or analyzed by "direct analysis". For this reason, samples are digested using the total recoverable mixed acid digestion before the determination of silver. For the analysis of samples containing higher concentrations of silver, succeeding smaller sample aliquots should be prepared until the analysis solution contains <0.1 mg/L silver.

Barium: For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

Physical interferences are effects associated with samples containing high dissolved solids or high acid concentrations. If physical interferences are present, diluting the sample or using some other appropriate compensation technique during the analysis may reduce them.

Method interferences are the result of contaminants in acids, reagents, glassware, and other sample processing hardware Running method blanks as described in Section 12 and 18

demonstrates the system is free of contamination. The analytical system must be free from contamination under the conditions of the analysis.

Boron: For accurate determination of boron in solid samples only quartz or PTFE beakers should be used during acid extraction. When possible, borosilicate glass should be avoided to prevent contamination of these parameters.

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined the SOP for ICP metals analysis, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements found in this method, to aid in determining whether this method is applicable to a given waste.

8. Safety

While digesting the samples, safety glasses should be worn due to splashing of the sample and concentrated nitric and hydrochloric acids.

Gloves should be worn to prevent samples and acids from coming in contact with the skin.

A lab coat should be worn to prevent acid from getting on clothes.

Use these reagents in a fume hood whenever possible. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples and all hot acid digestions must be done in a fume hood.

Other safety precautions should be conducted in accordance with the laboratory's Safety Manual. Other actions can also be applied if deemed necessary. A reference file of material safety data sheets (MSDS) is available to all personnel involved in an analysis using chemicals.

9. Equipment and Supplies

Hot Block Digestor, capable of maintaining a temperature of 95 +/-5 °C

Digestor Tubes with Screw Caps: 50 mL capacity, Class A Tolerance

Thermometers, glass, alcohol: capable of measuring temperatures ranging from 60 °C to 110 °C

Filtermate: disposable 2.0 micron filter apparatus for Digestor Tubes

Volumetric Pipettes, or equivalent Class A: 10 mL, 5 mL, 2 mL, and 1 mL

Repipettors: for use on all Trace metal grade acids

10. Reagents and Standards

Reagent water - Reagent water in the metals laboratory is water from the laboratory DI system. Analysis of laboratory blanks is a check on the quality of the water.

Nitric acid -Concentrated, Trace metal grade or equivalent.

Hydrochloric acid - Concentrated, Trace metal grade or equivalent.

Stock Standard- Stock standards are purchased and diluted to a working concentration, for all analytes that are to be digested using this method. **Matrix Spiking Solution** - Certified stock

standard solutions in nitric acid are prepared for use as matrix spiking solutions. This solution(s) is added to all required quality control samples (MS, MSD, LCS, LCSD)

Matrix spiking solutions are stored in plastic bottles at room temperature. These solutions must be replaced per vendor's expiration date. This expiration date is applicable to solutions purchased and used directly from the vendor's container.

For dilute matrix spiking solutions prepared from stock standards, the expiration date is six months from the date of preparation or prior to the manufacturer's expiration date.

11. Sample Collection, Preservation, Shipment and Storage

Samples that do not meet preservation requirements, minimum sample size or have or will exceed holding times:

Must be documented as such on the chain of custody.

The client must be notified and the deficiencies documented.

11.1 Sample Collection

Holding time: The holding time limitation is six months from the date of collection.

Minimum volume required: 50 mL

Bottle type: Plastic or Glass

11.2 Sample Preservation

Preservation: Aqueous samples require HNO3 acid preservation to a pH <2 before analysis.

Note: Those samples requiring dissolved metals are either field filtered and preserved or filtered at the laboratory prior to preservation.

When sample is to be analyzed that does meet the sampling or preservation requirements, note the exception to the requirement on the report and report the result value in brackets or other suitable qualifier symbol.

In consultation with the client the laboratory may define a project specific sample handling practice based on regulatory requirements.

11.4 Sample Storage

Aqueous samples may be stored at room temperature from time of sample receipt until analysis.

Maintain sample digestates at room temperature.

12. Quality Control

12.1 Laboratory Blank (LB)

A **laboratory blank** (also known as a **laboratory reagent blank**) shall be prepared and analyzed at a minimum of one per preparation batch of 20 or less samples per matrix type prepared over time. The method blank shall be processed through all preparatory steps used for the samples.

12.2 Laboratory Control Sample (LCS)

The LCS (also known as a laboratory fortified blank) shall be prepared and analyzed at a minimum of one per preparation batch of 20 or less samples per matrix type prepared over time. In accordance with the test method, the LCS is prepared containing all of target analytes.

If insufficient sample is available for an MS/MSD then prepare a LCS duplicate (LCSD) and analyze.

Some clients may require different spiking levels and/or target analytes; these specific needs are documented on the request for analysis forms.

12.3 Matrix Spike (MS)

The MS shall be prepared and analyzed at a minimum of one per preparation batch of 20 or less samples per matrix type prepared over time. The selected samples shall be rotated among client samples (unless otherwise directed by the client) so that various matrix problems may be noted and/or addressed. In accordance with the test method, the MS is prepared containing all the of target analytes.

Some clients may require different spiking levels and/or target analytes, these specific needs are documented on the request for analysis forms.

12.4 Matrix Spike Duplicates (MSD)

A Matrix Spike Duplicate shall be prepared and analyzed at a minimum of one per preparation batch of 20 or less samples per matrix type prepared over time. The RPD between the MS and MSD is calculated for the statement of method precision. Duplicates of field samples or of the LCS shall be prepared in compliance with client directives as long as the client specifications are more stringent than the reference method criteria.

13. Calibration and Standardization

13.1 Thermometers

Check the thermometer to ensure the calibration is not expired. Check the thermometer during the digestion and record the temperature in the digestion logbook. Be certain that any correction factor is noted in the logbook.

13.2 Balances

All balances are verified each day by the quality control department. Ensure that balance calibration has not expired prior to use.

13.3 Pipettors

Be sure all adjustable pipettors are calibrated each day prior to use, and the data is recorded in the proper logbook.

14. Sample Preparation

Record the sample number (standard or QC sample identifier), preparation batch identifier, standard solution identifier, dilution, analyst initials, deviations from this procedure and visual observations on the metal prep worksheet.

Samples digested in a batch must include a method blank (MB), laboratory control sample (LCS), matrix spike and matrix spike duplicate sample (MS/MSD).

All samples and QC samples must be digested in the same operational manner.

Perform a preliminary review of the nature of the sample. Record on worksheet any unusual sample characteristics such as color, presence of an oily sheen, debris in the sample, limited sample size, etc. Note any problems in obtaining a representative aliquot of the sample.

1. Total Recoverable Metals Mix the sample thoroughly to achieve homogeneity by inverting numerous times.. For each sample digestion procedure measure 50 mL of sample directly into the Class A digestion tube.

2. Add 1 mL of HNO_3 and 2.5 mL of HCl and mix. Heat the sample in the digestion block to 90 - 95°C and digest to a volume of 10-20 mL,without boiling.
3. Allow the sample to cool and be dilute to 50 mL.. The sample is now ready for analysis by ICP-AES or ICP-MS. Note: If the solids have not settled at time of analysis, the sample will be filtered using a 2.0 micron filtermate.

14.1 Analytical Sequence

The sample preparation batch must include:

LB
LCS
Sample 1
Sample 1 MS/MSD
Additional project or client specific QC samples, such as LCSD or sample duplicate

15. Calculations

Calculations are not applicable for this preparatory procedure.

16. Method Performance

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix.

16.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure. The mixed standard LCS solution and/or individual element LCS solutions may be used as the QC solution. Analyze four aliquots of the LCS according to the preparation method. Calculate the standard deviation of the four results (Sx) in mg/L, the relative standard deviation (%RSD = 100% * Sx/X) the average result for the four aliquots (X) in mg/L, and the percent recovery (R) in % using the four results

Acceptance limits for %R are: 100 ± 15% of the theoretical value. Acceptance limit for %RSD is: 10% RSD.

16.2 Comparison to Reference Method Data

Quality Control sample performance acceptance limits are summarized in the ICP Analytical SOP

16.3 In-House Control Limits

Quality Control sample performance acceptance limits are summarized in the ICP Analytical SOP

17. Pollution Prevention

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the laboratory waste disposal program and applicable waste disposal regulations. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycling or waste from the facility.

18. Data Assessment and Criteria For Quality Control Measures

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample matrix spikes indicate atypical method performance, a Laboratory Control Sample (LCS) is used to confirm the measurements were performed in an in-control mode of operation.

Data Assessment and Criteria for Quality Control Measures are summarized in the ICP Analytical SOP

18.1 Blanks

Data Assessment and Criteria for Quality Control Measures are summarized in the ICP Analytical SOP

18.2 Laboratory Control Sample (LCS)

Data Assessment and Criteria for Quality Control Measures are summarized in the ICP Analytical SOP

18.3 Matrix Spikes and Matrix Spike Duplicates (MSMSD)

Data Assessment and Criteria for Quality Control Measures are summarized in the ICP Analytical SOP

19. Corrective Actions for Out-Of-Control Data

The process for handling corrective actions is found in the laboratory's Quality Manual Section 5.6.

20. Contingencies for Handling Out-Of-Control Or Unacceptable Data

Improper preservation and improper storage are noted on the corrective action form and included in the final report. Review of the Method Blank analysis, LCS recovery, matrix spike recovery, sample duplicate RPD for acceptable performance occurs for each batch of samples. Record any trends or

performance abnormalities on a corrective action form. Qualify all results not meeting the laboratory-defined criteria in the client report.

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples. When this is not possible, the Technical Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualifiers, are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and a discussion of the rationale for reporting.

The process for handling unacceptable and out of control data is found in the laboratory QM Section 9. The reporting of data that is out of control must be approved and documented by Quality Assurance Officer and the Technical Director.

21. Waste Management

The laboratory Safety Manual identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with Section 11.5 of the laboratory QM.

22. References

Method 3005A, 3010A, and 3050B of EPA Manual SW-846 Third Edition (through Update III) December 1996

40 CFR Part 136 Appendix B, Procedure for the Determination of the Method Detection Limit

A&L Quality Manual, current edition

ICP Analytical SOP

23. Tables, Diagrams, Flowcharts and Validation Data

Metals Prep template is found in the Quality System electronic files.

Standard Operating Procedure

For

Acid Digestion of Solids for Metals Analysis EPA SW-846 3050B

Prepared by: S. Hanson_____ (signature)

Technical Director: M. Kauffman _____(signature)

1. Identification of Test Method

Acid Digestion of Solids for Metals Analysis. The laboratory records and reports refer to this analysis as 3050B. This SOP based on metal preparation procedures of EPA SW-846 Method 3050B, Acid Digestion of Sediments, Sludges, and Soils.

2. Applicable Matrix or Matrices

This method is applicable to solid samples. Nitric acid digestates of soil, sediment, and plant tissue are prepared using this method. Analytes other than those listed in the scope and application section may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest.

3. Detection Limits

The laboratory follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. Additionally, the laboratory determines the MDL whenever there is a significant change in equipment or substantive revision of the technical protocols for preparation and analysis of samples by this test method. The relative significance and substantiveness of any changes to equipment or protocols that may require redetermination of the MDLs shall be decided, and documented in QA files, by the QA Officer in conjunction with technical assistance from the laboratory Technical Director. All processing steps of the analytical method, including any routine preparation steps, are included in the determination of the MDL. The MDLs measured by the laboratory are on file for review in each determinative analytical procedure. All supporting documentation used in the determination of the laboratory MDLs is maintained in the laboratory QA files. These may include but are not limited to, laboratory prep batch worksheets, instrument printouts or Quantitation reports and MDL calculation spreadsheets.

The laboratory determined MDL must always be less than or equal to the reference method MDL. For those cases in which a regulatory compliance limit is in effect, the laboratory MDL must be less than one-third of the compliance limit.

MDL Check Samples are analyzed on a quarterly basis to verify the reported MDL when state or regulatory agencies require such.

4. Scope and Application

This method is applicable to the preparation of solid matrices for measurement of metals at various reporting levels depending upon the instrumentation used for analysis. This SOP is written for metals analysis using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Parameter List by Method and Matrix

Parameter	CAS
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Boron (B)	7440-42-8
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-98-7
Nickel (Ni)	7440-02-0
Phosphorus (P)	7723-14-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silica (SiO_2)	7631-86-9
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Thallium (Tl)	7440-28-0
Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6
Sulfur (S)	63705-05-5

The parameter list is extended to add metals commonly requested by clients for solid waste samples such as soil, sludge and other acid digestible materials.

For the determination of total recoverable parameters in solid samples a digestion is required prior to analysis.

5 Summary of Test Method

Various sample processing techniques must be considered and addressed appropriately for the parameters of interest including; total parameters using hot acid digestion techniques, and control of interferences. Sample processing includes the acid digestion of an accurately weighed or measured sample aliquot of a well mixed, homogeneous solid sample. The acid concentration and acids selected in the sample preparation step must be the same as the standards used for instrumentation calibration

For the digestion of samples, a representative 1-2 g sample is digested with repeated additions of nitric acid, hydrochloric acid and hydrogen peroxide. The resultant digestate is diluted to a final volume of 50 mL and either filtered or allowed to settle prior to the analytical procedure.

6. Definitions

The laboratory Quality Manual contains the definitions of standard terms used in this SOP. Additional terms are defined below.

Total Metals—The concentration determined on an unfiltered sample following vigorous digestion.

Note: Method 3050B is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure, as they are not usually mobile in the environment. If absolute total digestion is required use Method 3052.

Total Recoverable Metals—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid. The concentrations of analytes determined by this procedure is commonly known as total recoverable metals

7. Interferences

Several types of interference effects may contribute to inaccuracies in the determination of trace elements. From the perspective of sample digestion, they can be summarized as follows:

Chemical Interferences are effects by a chemical or group of chemicals that cause the measurement of a target chemical or analyte to be incorrect

Silver: Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, spiked sample matrices and spiked blanks or as a dissolved parameter or analyzed by "direct analysis". For this reason, samples are digested using the total recoverable mixed acid digestion before the determination of silver. For the analysis of samples containing higher concentrations of silver, succeeding smaller sample aliquots should be prepared until the analysis solution contains <0.1 mg/L silver. The extraction of solid samples containing concentrations of silver >50 mg/kg should be treated in a similar manner.

Barium: For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

Physical interferences are effects associated with samples containing high dissolved solids or high acid concentrations. If physical interferences are present, diluting the sample or using some other appropriate compensation technique during the analysis may reduce them.

Method interferences are the result of contaminants in acids, reagents, glassware, and other sample processing hardware. Running method blanks as described in Section 12 and 18 demonstrates the system is free of contamination. The analytical system must be free from contamination under the conditions of the analysis.

Boron: For accurate determination of boron in solid samples only quartz or PTFE beakers should be used during acid extraction. When possible, borosilicate glass should be avoided to prevent contamination of these parameters.

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined the SOP for ICP metals analysis, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements found in this method, to aid in determining whether this method is applicable to a given waste.

8. Safety

While digesting the samples, safety glasses should be worn due to splashing of the sample and concentrated nitric and hydrochloric acids.

Gloves should be worn to prevent samples and acids from coming in contact with the skin.

A lab coat should be worn to prevent acid from getting on clothes.

Use these reagents in a fume hood whenever possible. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples and all hot acid digestions must be done in a fume hood.

Other safety precautions should be conducted in accordance with the laboratory's Safety Manual. Other actions can also be applied if deemed necessary. A reference file of material safety data sheets (MSDS) is available to all personnel involved in an analysis using chemicals

9. Equipment and Supplies

Hot Block Digestor, capable of maintaining a temperature of 95 +/-5 °C

Digestor Tubes with Screw Caps: 50 mL capacity, Class A Tolerance

Balance capable of weighing to 0.01 g

Thermometers, glass, alcohol: capable of measuring temperatures ranging from 60 °C to 110 °C

Filtermate: disposable 2.0 micron filter apparatus for Digestor Tubes

Volumetric Pipettes, or equivalent Class A: 10 mL, 5 mL, 2 mL, and 1 mL

Repipettors: for use on all Trace metal grade acids

10. Reagents and Standards

Reagent water - Reagent water in the metals laboratory is water from the laboratory DI system. Analysis of laboratory blanks is a check on the quality of the water.

Nitric acid -Concentrated, Trace metal grade or equivalent.

Hydrochloric acid - Concentrated, Trace metal grade or equivalent.

Hydrogen peroxide – 30% H_2O_2

Stock Standard- Stock standards are purchased and diluted to a working concentration, for all analytes that are to be digested using this method. **Matrix Spiking Solution** - Certified stock standard solutions in nitric acid are prepared for use as matrix spiking solutions. This solution(s) is added to all required quality control samples (MS, MSD, LCS, LCSD)

Matrix spiking solutions are stored in plastic bottles at room temperature. These solutions must be replaced per vendor's expiration date. This expiration date is applicable to solutions purchased and used directly from the vendor's container.

For dilute matrix spiking solutions prepared from stock standards, the expiration date is six months from the date of preparation or prior to the manufacturer's expiration date.

11. Sample Collection, Preservation, Shipment and Storage

Samples that do not meet preservation requirements, minimum sample size or have or will exceed holding times:

Must be documented as such on the chain of custody.

The client must be notified and the deficiencies documented.

11.1 Sample Collection

Holding time: The holding time limitation is six months from the date of collection.

Minimum volume required: 4 oz.

Bottle type: Plastic or Glass

11.2 Sample Preservation

Preservation: Solid samples require no chemical preservation before analysis. Solid samples require ice or refrigeration from the time of collection until analysis. Cool and maintain the sample temperature between 2 and 6 °C from time of sample receipt until analysis.

When sample is to be analyzed that does meet the sampling or preservation requirements, note the exception to the requirement on the report and report the result value in brackets or other suitable qualifier symbol.

In consultation with the client the laboratory may define a project specific sample handling practice based on regulatory requirements.

11.4 Sample Storage

Solid samples are stored between 2 and 6 °C from time of sample receipt until analysis.

Maintain sample digestates at room temperature.

12. Quality Control

12.1 Laboratory Blank (LB)

A **laboratory blank** (also known as a **laboratory reagent blank**) shall be prepared and analyzed at a minimum of one per preparation batch of 20 or less samples per matrix type prepared over time. The method blank shall be processed through all preparatory steps used for the samples.

12.2 Laboratory Control Sample (LCS)

The LCS (also known as a laboratory fortified blank) shall be prepared and analyzed at a minimum of one per preparation batch of 20 or less samples per matrix type prepared over time. In accordance with the test method, the LCS is prepared containing all of target analytes.

If insufficient sample is available for an MS/MSD then prepare a LCS duplicate (LCSD) and analyze.

Some clients may require different spiking levels and/or target analytes, these specific needs are documented on the request for analysis forms.

12.3 Matrix Spike (MS)

The MS shall be prepared and analyzed at a minimum of one per preparation batch of 20 or less samples per matrix type prepared over time. The selected samples shall be rotated among client samples (unless otherwise directed by the client) so that various matrix problems may be noted and/or addressed. In accordance with the test method, the MS is prepared containing all the of target analytes.

Some clients may require different spiking levels and/or target analytes, these specific needs are documented on the request for analysis forms.

12.4 Matrix Spike Duplicates (MSD)

A Matrix Spike Duplicate shall be prepared and analyzed at a minimum of one per preparation batch of 20 or less samples per matrix type prepared over time. The RPD between the MS and MSD is calculated for the statement of method precision. Duplicates of field samples or of the LCS shall be prepared in compliance with client directives as long as the client specifications are more stringent than the reference method criteria.

13. Calibration and Standardization

13.1 Thermometers

Check the thermometer to ensure the calibration is not expired. Check the thermometer during the digestion and record the temperature in the digestion logbook. Be certain that any correction factor is noted in the logbook.

13.2 Balances

All balances are verified each day by the quality control department. Ensure that balance calibration has not expired prior to use.

13.3 Pipettors

Be sure all adjustable pipettors are calibrated each day prior to use, and the data is recorded in the proper logbook.

14.1 Sample Preparation

Record the sample number (standard or QC sample identifier), preparation batch identifier, standard solution identifier, dilution, analyst initials, deviations from this procedure and visual observations on the metal prep worksheet.

Samples digested in a batch must include a method blank (MB), laboratory control sample (LCS), matrix spike and matrix spike duplicate sample (MS/MSD).

All samples and QC samples must be digested in the same operational manner.

Perform a preliminary review of the nature of the sample. Record on worksheet any unusual sample characteristics such as color, presence of an oily sheen, debris in the sample, limited sample size, etc. Note any problems in obtaining a representative aliquot of the sample.

1. Mix the sample thoroughly to achieve homogeneity using a tongue blade. For each digestion procedure, weigh to the nearest 0.01g a minimum of 1.00g sample into a digestion tube.

2. Add 2.5 mL of HNO_3 and 2.5 mL of DI and mix. Heat the sample in the digestion block to 95°C ± 5°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 2.5 mL of concentrated HNO_3 and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3 repeat this step (addition of 2.5 mL of conc. HNO_3) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times. After the two hours, remove the sample from the hotblock and allow to cool.

3. After the sample has cooled, add 1 mL of water and 1.5 mL of 30% H_2O_2 Allow the sample to heat until reaction occurs. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the vessel.

4. Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

5. Continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. Maintain a covering of solution over the bottom of the vessel at all times. Note: If the sample digestate is to be analyzed by ICP-MS it may be cooled and diluted to 50 mL at this time. Note: If the solids have not settled at time of analysis, the sample will be filtered using a 2.0 micron filtermate.

6. If sample is to be analyzed by ICP-AES add 5 mL conc. HCl to the sample and heat at 95° C ± 5°C for 15 minutes.

7. Allow the sample to cool and be dilute to 50 mL. The sample is now ready for analysis by ICP-AES. Note: If the solids have not settled at time of analysis, the sample will be filtered using a 2.0 micron filtermate.

14.4 Analytical Sequence

The sample preparation batch must include:

LB
LCS
Sample 1
Sample 1 MS/MSD
Additional project or client specific QC samples, such as LCSD or sample duplicate

15. Calculations

Calculations are not applicable for this preparatory procedure.

16. Method Performance

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix.

16.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure. The mixed standard LCS solution and/or individual element LCS solutions may be used as the QC solution. Analyze four aliquots of the LCS according to the preparation method. Calculate the standard deviation of the four results (Sx) in mg/L, the relative standard deviation (%RSD = 100% * Sx/X) the average result for the four aliquots (X) in mg/L, and the percent recovery (R) in % using the four results.

Digested solid samples (aqueous samples that have undergone the solids digestion procedure): Acceptance limits for %R are: 100 ± 15% of the theoretical value. Acceptance limit for %RSD is: 10% RSD.

16.2 Comparison to Reference Method Data

Quality Control sample performance acceptance limits are summarized in the ICP SOP 03.02.0046.

16.3 In-House Control Limits

Quality Control sample performance acceptance limits are summarized in the ICP SOP 03.02.0046.

17. Pollution Prevention

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the laboratory waste disposal program and applicable waste disposal regulations. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycling or waste from the facility.

18. Data Assessment and Criteria For Quality Control Measures

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample matrix spikes indicate atypical method performance, a Laboratory Control Sample (LCS) is used to confirm the measurements were performed in an in-control mode of operation.

Data Assessment and Criteria for Quality Control Measures are summarized in the ICP SOP 03.02.0046.

18.1 Blanks

Data Assessment and Criteria for Quality Control Measures are summarized in the ICP SOP 03.02.0046.

18.2 Laboratory Control Sample (LCS)

Data Assessment and Criteria for Quality Control Measures are summarized in the ICP SOP 03.02.0046.

18.3 Matrix Spikes and Matrix Spike Duplicates (MSMSD)

Data Assessment and Criteria for Quality Control Measures are summarized in the ICP SOP 03.02.0046.

19. Corrective Actions for Out-Of-Control Data

The process for handling corrective actions is found in the laboratory's Quality Manual Section 5.6.

If the LCS recovery falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory defined criteria.

Review standards preparation logbooks Check all calculations and ensure dilution factors are properly recorded. Re-prepare the LCS sample to identify possible preparation errors of the LCS. Re-digest the samples when the LCS is not within acceptable limits.

Check the digestion logbook sequence to ensure that all samples were entered in the proper order and were labeled correctly.

Check the digestion logbook for any comments or qualifiers concerning the sample or the analytical batch

Record all hotplate adjustments and maintenance in the digestion logbook.

20. Contingencies for Handling Out-Of-Control Or Unacceptable Data

Section 18.8 addresses situations that may generate out-of-control or unacceptable data.

Improper preservation and improper storage are noted on the corrective action form and included in the final report. Review of the Method Blank analysis, LCS recovery, matrix spike recovery, sample duplicate RPD for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a corrective action form. Qualify all results not meeting the laboratory-defined criteria in the client report.

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples. When this is not possible, the Technical Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and a discussion of the rationale for reporting.

The process for handling unacceptable and out of control data is found in the laboratory QM Section 9. The reporting of data that is out of control must be approved and documented by Quality Assurance Officer and the Technical Director.

21. Waste Management

The laboratory Safety Manual identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with Section 11.5 of the laboratory QM.

22. References

Method 200.7 Revision 4.4 of Methods for the Determination of Metals in Environmental Samples Supplement I EPA/600/R-94-111 May, 1994

Method 3005A, 3010A, and 3050B of EPA Manual SW-846 Third Edition (through Update III) December 1996

Method 7000A of EPA Manual SW-846 Third Edition (through Update III) December 1996

40 CFR Part 136 Appendices B, Current edition

A&L Quality Manual, current edition

ICP SOP 03.02.0046

23. Tables, Diagrams, Flowcharts and Validation Data

Metals Prep template is found in the Quality System electronic files.

AFFIDAVIT 8772140

A & L Analytical Laboratories, Inc.
411 North Third Street
Memphis, TN 38105-2723

Standard Operating Procedure

QC

Title: Organic Carbon and Organic Matter

S.O.P. Number: 05.01.0030.01

Reference:

Effective Date:

Revision No.

Reviewed By: _____ Title:

_____

_____

Approved by: _____ Title:

_____

8772141

Title: Organic Carbon and Organic Matter
S.O.P.# 05.01.0030.01
Pages: 1 of 3

1.0 PURPOSE

To outline the procedures necessary to perform organic carbon and organic matter determinations on soils using the Walkley-Black method for A&L personnel.

2.0 SCOPE

This method quantifies the amount of oxadizable soil carbon as determined by reaction with Cr_2O_7 and sulfuric acid. The unreacted dichromate is titrated with $FeSO_4$, using Ortho-phenanthroline as an indicator, and organic carbon is derived from the difference. Since, not all of the organic carbon in the sample is oxidized, the value is considered an estimate.

The method detection limit is 0.10% and can generally be reproduced with in ± 10%.

3.0 SAMPLE HANDLING

Samples should be prepared for analysis by drying the sample at 105C and grinding it to pass through a 40 mesh sieve according to the protocol outlined in A&L SOP 05.03.0002.00

4.0 INTERFERENCE

Some of the organic carbon might not completely oxidize. The value calculated is considered an estimate. For samples with large amounts of carbon, a form of dry combustion might be considered.

5.0 SAFETY

When handling and mixing reagents, appropriate eyewear and gloves should be worn. When mixing the sulfuric acid and chromate solution, make sure it is performed under a fume hood.

6.0 REAGENTS

6.1 Deionized water

6.2 Potassium Dichromate solution, 1.0 N: Dissolve 49.04 g of Primary Standard Grade $K_2Cr_2O_7$ (dried at 105 C at least 2 hours) in DI water and dilute to 1000ml.

6.3 Ferrous Sulfate-Heptahydrate solution, 0.5 N: Dissolve 140 g of $FeSO_4*7H_2O$ in 500 ml of DI, add 15.0 ml of conc. H_2SO_4 and dilute to 1000 ml.

6.4 Concentrated Sulfuric acid. (Approx. 36 N).

6.5 Ortho-phenanthroline-ferrous complex soln., 0.025 M. Dissolve 3.71 g of O-phenanthroline monohydrate and 1.74 g of $FeSO_4*7H_2O$ in DI and dilute to 250 ml. Store in plastic bottle.

6.6 Carbon Standard, 1mg/1ml. In a 1L volumetric flask, dissolve 2.38 g of Sucrose in 800 ml DI, dilute to vol and mix. 1ml=1mg C.

7.0 EQUIPMENT

7.1 Analytical Balance: 100 g capacity, ± 0.001
7.2 Erlenmeyer Flask 500 ml
7.3 Volumetric pipets, 5-20 ml
7.4 Mohr pipet, 25 ml
7.5 50 ml burette with graduations of 0.1 ml
7.6 100 ml graduate cyclinder

8.0 PROCEDURE

8.1 Weigh 0.5 ± 0.005 g of prep sample into 500 ml Erlenmeyer flask. Include a blank soln.
8.2 Volumetrically pipette 10 ml of 1.0 N $K_2Cr_2O_7$ to each flask, including the blank.
8.3 Using a Mohr pipette, add 20 ml of conc. H_2SO_4 to each flask, including the blank.
8.4 Swirl the flask for appr. 1 min and allow to cool on a heat resistant surface for 30 min.
8.5 Add 100 ml of DI water.
8.6 Add 2-3 drops of Ortho-phenanthroline indicator.
8.7 Titrate with $FeSO_4$. As you get closer to the endpoint, the color will change from greenish tint to a blue green tint.
8.8 Add 2-3 more drops of the indicator.
8.9 Continue dropwise titration to reddish wine color endpoint.
8.10 Record amount of $FeSO_4$ used.
8.11 Calculations:

8.11.1 Normality $FeSO_4$ = (ml $K_2Cr_2O_7$* N $K_2Cr_2O_7$)/ ml $FeSO_4$ – Blank

8.11.2 meq $FeSO_4$ = ml $FeSO_4$ * N $FeSO_4$

8.11.3 Organic Carbon (%) = $\frac{((\text{meq } K_2Cr_2O_7 - \text{meq } FeSO_4)*0.399)-\text{blank}}{\text{sample wt}}$

8.11.4 Organic Matter (%) = 1.72 * Organic Carbon %

$N K_2Cr_2O_7$ + mL KCr_2O_7 / 1 * 10

9.0 METHOD PERFORMANCE

9.1 Analyze a reagent blank with each batch of 20 or fewer.
9.2 Analyze at least one blank spike sample with each batch of 20 or fewer. Use 20 ml aliquot of the Carbon Standard as the spike. Add spiking material before digesting.

$N FeSO_4 = (10 * 1) / (\frac{10}{21} + 1)/21 = 0.476$

meq $FeSO_4 = \frac{18.6}{21} * 0.476 = 8.85$

9.3 Analyze at least one duplicate sample for every batch of 20 or fewer. A duplicate sample is a second weighing of a sample that is processed completely as a separate sample.

9.4 Analyze at least one duplicate spike sample with each batch of 20 or fewer. A duplicate spike is a third weighing of the duplicated sample that is spiked with 20 ml of the Carbon Standard. Spike material is added with the sample is weighed and is processed like a separate sample.

10.0 DATA ASSESMENT AND ACCEPTANCE CRITERIA FOR QC MEASURES

10.1 The reagent blank should recover 0-0.50 mg carbon.

10.2 The blank spike should have a recovery of 95.0-105% of the actual value.

10.3 Duplicate analyses should have a %RSD of less than or equal to 5.0%.

10.4 Duplicate spike analyses should have a recovery of 95.0-105% of the actual value

11.0 CORRECTIVE ACTION

All data assessment and acceptance criteria must be met before the results for an analytical batch run can be validated. Consult with laboratory management for assistance in determining possible sources of error.

8772144

Total Organic Carbon by Combustion-Infrared Method

SM 5310B and EPA 415.1

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

This method includes the measurement of organic carbon in drinking, surface, and saline waters, domestic and industrial wastes. The method is most applicable to measurement of organic carbon above 1 mg/L.

The accuracy of this method is dependent on particle size reduction due to the fact that micro-liter syringes are used to introduce the sample.

2.0 Summary of Method

The sample is diluted if necessary and injected into a heated reaction chamber packed with an oxidative catalyst of platinum. The water is vaporized and the organic carbon is oxidized to CO2. The CO2 from oxidation of organic and inorganic carbon is transported in the carrier-gas stream and is measured by an infrared analyzer.

Because total carbon is measured, inorganic carbon (IC) must be measured separately and TOC obtained by the difference.

The IC is measured by injecting the sample into a separated injection port with no oxidative catalyst. All IC is converted to CO2, which is measured by an infrared analyzer. Under these conditions organic carbon is not oxidized and only IC is measured.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts of interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and solvents may be necessary.

3.1.1 Glassware contamination can result in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem. Chromic acid that is not completely rinsed will cause similar problems with analyte degradation and should be carefully rinsed to avoid this problem. Refer to the SOP for cleaning of laboratory glassware: Sogcln03.doc.

3 1.2 Removal of carbonate and bicarbonate by acidification and purging results in the loss of volatile organic substances. Therefore the method of sparging is not recommended. The volatiles also can be lost during sample dilution if the temperature is allowed to rise.

3.1.3 Another important loss can occur if large carbon-containing particles fail to enter the syringe needle for injection.

3.1.4 If any problem arises during the analysis, the analyst should note the circumstances on the analytical data sheet.

4.0 Equipment and Apparatus

4.1 Equipment

4.1.1 Dohrmann Model Apollo 9000 coupled with autosampler

5.0 Reagents and Standards

5.1 Policy.

5.1.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may

be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents/solvents/standards must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

5.1.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Program (SVQAP). This program is detailed in the Quality Assurance Program Plan Section 6.3. Refer to SOP Qasrpt02.doc, "*Standard and Reagent Preparation and Traceability*".

5.2 Reagents

5.2.1 Deionized water

5.2.2 Compressed air: 99.98 % purity

Phosphoric acid, 80%

5.3 Solutions/Standards

Potassium phthalate standard (100 mg/L): 0.2128 g KHP diluted to 1 L with DI

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

6 1.1 Refer to Standard Methods and EPA Manual for guidance concerning containers, preservation and holding times.

6.2 Holding Times

6.2.1 Holding Time for extraction is defined as the number of days from ***Sample Collection*** (e g Sample Date) to extraction.

6 2.2 The holding time for this analysis is 28 days, preserved with sulfuric acid to a pH of less than 2, and maintained at a temperature of 4° C.

7.0 Procedure

7 1 Set instrument on ready mode

7.2 Adjust analyzer oxygen flow to 200 +/- 20 mL/min.

7 3 Set furnace temperature at 680°C.

7.4 When baseline has stabilized, run 4 or 5 reps of cleaning procedure

7.5 System holds calibration from day to day when used frequently. Check calibration by analyzing a blank and a mid-range check standard to verify that the instrument calibration is still valid. Analyze another standard from a second source to independently verify the verification curve. If these standards are within acceptance range, proceed with sample analysis. If not, recalibrate the analyzer using a system blank and the series of standards in the CALIBRATION program (1, 10, 25 and 100 mg/L).

7.6 For aqueous samples, fill a 40-ml vial with sample. The autosampler will take an appropriate amount of aliquot from this vial. For soil samples, leach 2.0 grams into 200 ml deionized water by stirring for one hour. Most samples will decant clearly, allowing enough sample volume to be withdrawn for analysis If samples will not decant, they must be filtered before analysis and a filter blank must be analyzed if this filtration is necessary.

7.7 Analyze samples in the TOC, 1-100 mg/L range. The instrument sparges away the inorganic carbon, so that only total organic carbon is reflected in the final result

7.8 All samples, matrix spikes and matrix spikes duplicates should be analyzed in duplicate, and the reported result will be the average of these analyses.

7.9 Retain the printout, which is properly labeled, dated and signed.

8.0 Quality Control/Quality Assurance/Corrective Action

8.1 A method/reagent blank is carried through the entire procedure and recorded on the work sheet on a daily basis.

8.2 Samples are analyzed in duplicate to determine reproducibility.

8.3 A matrix spike and matrix spike duplicate are analyzed every analytical batch (10 samples) or daily, whichever is more frequent.

8.4 Control limits are available and will be recorded on the QC sheet. If any quality control data (ie. duplicate or matrix spike) fall outside the QC limits, the analyst MUST notify the supervisor IMMEDIATELY. All deviations MUST be noted on the QC data sheet as well as the corrective actions. The QC Officer MUST be notified of all infractions.

8.5 All reagents must be recorded on the Standard Log Book and will be labeled with a Standard Reference Number.

8.6 This number is unique and must be recorded on all work sheets to allow traceability.

8.7 Analyze a filter blank when ever samples are filtered.

8.8 Analyze an independent mid-range check standard from an independent source with each analytical batch.

9.0 Calculations

The instrumentation provides a direct mg/L TOC measurement. The reported result is the average of all replicates (duplicate or quadruplicate), adjusted for any dilution factor.

10.0 Data Validation

Refer to the Laboratory's Quality Manual for details.

11.0 Waste Management

Refer to the Waste Management Plan.

12.0 Health and Safety

Consult the Chemical Hygiene and Laboratory Safety Plans..

13.0 Training & Training Validation

Reference the Employee Training Standard Operating Procedure.

14.0 References

14.1 *"Carcinogens – Working with Carcinogens"*, Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

14.2 "OSHA Safety and Health Standards, General Industry", 29 CFR 1910.

14.3 *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.

14.4 *"Safety in Academic Chemistry Laboratories"*, American Chemical Society Publication, Committee on

Chemical Safety.

14.5 Standard Methods, 18th Edition.

14.6 Code of Federal Regulations 40 CFR Part 136.

14.7 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements, Appendix H.

14.8 EPA, Methods for the Chemical Analysis of Water and Waste, EPA 600-4-79-020.

15.0 Appendix

8772150

Determination of Anions using

Ion Chromatography according to EPA Method 300.0

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application for Method

1.1 To address the determination of seven inorganic anions *by EPA Method 300.0 Revision 2.1. Method A* is chosen for this determination. Applicable Matrices: Drinking water, surface water, mixed domestic and industrial wastewaters, groundwaters, reagent waters, solids (after extraction) and leachates.

1.2 Analytes that are currently reported using this method are listed in Section 6.4.2, Figure 1.

1.3 Detection limits for the analytes currently reported using this method are listed in the Table 8. Refer to Determination of MDL/MQL/RL SOP for further information on detection limits.

2.0 Summary of Method

2.1 A small volume of sample, 5 mL, is loaded onto an automated auto-sampler, where the sample is filtered through a 0.45-µm membrane and loaded in a 25-µL loop. The sample is introduced into the ion chromatograph, where the ions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector. Sample quantitation is based on comparing sample concentration with a standard curve.

2.2 An extraction/dilution procedure must be performed for solid samples, or industrial samples.

3.0 Interferences and Potential Problems

3.1 Refer to *Section 4.0 of EPA Method 300.0* for additional details.

3.2 Method interferences are reduced by proper glassware cleaning procedures. Cleaning procedures are detailed in SOP Inorganic Glassware Cleaning Procedures.

3.3 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution can be used to solve most interference problems associated with retention times.

3.4 The water dip or negative peak that elutes near, and can interfere with the fluoride peak is eliminated by the use of Dionex columns, specifically designed to address this interference.

3.5 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in the chromatograms.

3.6 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere.

3.7 The acetate ion elutes early during the chromatographic analysis. Therefore, this method is not allowed for TCLP leachates where acetic acid is used for pH adjustments.

3.8 Analyses of calibration and reagent blanks provide information about the presence of contaminants. Subtracting blank values from sample results is not permitted.

4.0 Equipment, Instrumentation and Apparatus

4.1 Analytical Systems – The current configuration of analytical systems for this method are found in Table 1

4.2 Refer to *Section 6.0 of EPA Method 300.0*

4.3 Glassware – (Vendor/Cat #).

4.4 Analytical balance capable of weighing 0.0001g.

5.0 Reagents and Standards

5.1 Refer to Section 7.0 of EPA Method 300.0.

5.2 Reagent grade chemicals are to be used for this method. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.3 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Procedure (SVQAP).

5.4 Reagents – Table 5

5.5 Stock Certified Solutions – Table 2 - Whenever possible, standard solutions are purchased as certified solutions from an outside source. Each solution is accompanied by certification data on the purity, precision, and traceability of the solution.

5.6 When a certified solution is not available, then the analyst must prepare a stock standard solution reference material of known purity using the procedures detailed in in Reagent and Standard Solutions Validation SOP.

5.7 Calibration Standards

5.8 The initial calibration is performed using five calibration standards (e.g., WS-1, WS-2). One standard corresponds to the MQL. The remaining standards encompass the working range of the method. All quantitatively reported analytes must be included in the calibration standards Table 2 details the certified solutions currently used. Table 6 details the preparation of the working standards from the certified solutions. Unopened stock solutions are valid for 6 months and one month for nitrite and phosphate; or as stated on the containers Opened solutions expire after one month.

5 9 Laboratory Control Solution - This standard contains all target analytes and is added to a clean matrix (i.e. blank spike) to monitor overall method performance. Table 2 details the certified solutions currently used. LCS standard preparation is listed in Table 5. Spiking volumes and concentrations are listed in Table 4.

5.10 Matrix Spike Solution - This solution contains all target analytes and is added to aliquots of sample (MS/MSD) to monitor sample matrix effects. Table 2 details the certified solutions currently used. MS standard preparation is listed in Table 5. Spiking volumes and concentrations are listed in Table 4. These solutions are to be prepared weekly.

6.0 Sample Preservation and Containers

6.1 Refer to *Section 8.0 of EPA Method 300.0.*

6.2 As a rule, LMP, Inc. does not engage in sampling activities and may not have control of field sampling activities conducted by clients However, each analytical method has specific container and preservation (chemical and/or temperature) requirements, which are essential to ensure the validity of the laboratory's data.

6.3 This technical standard operating procedure must contain information regarding the preservation requirements and recommended containers for the samples, as it pertains to a specific analysis. Refer to LMP's Sample Login Procedures SOP for requirements concerning containers and preservation requirements.

6.4 The holding time for the specific method must be documented in the standard operating procedure. The holding time begins at the onset of taking a sample, not when it arrived at the laboratory. Refer to the LMP's Sample Login Procedures SOP for holding time requirements Holding time for extraction is defined as the number of days from sample collection (e.g , sample date) to extraction.

6.4.1 Holding time for analysis is defined as the number of days from sample extraction in the laboratory to date injected/analyzed by the instrument.

6.4.2 Figure 1 below lists sample preservation and holding times for the anions.

Figure 1 - Preservation and Holding Times

Analyte	Preservation	Holding Time
Bromide	None required	28 days
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Nitrite-N	Cool to 4°C	48 hours
Nitrite/Nitrate N	H_2SO_4 pH < 2	28 days
Phosphate	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

Note: **If the determined value for a sulfuric preserved combined nitrate/nitrite exceeds 0.5 mg/L as N, a resample with no preservation must be analyzed for the individual concentrations of nitrate and nitrite.**

6.5 The method of preservation and the holding time for sample analysis are determined by the anions of interest. The anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. All samples will be stored at 4°C for all analytes of interest.

7.0 Calibration and Standardization

7.1 Refer to Section 10.0 of EPA Method 300.0.

7.2 Ion chromatographic operating parameters for MDL and retention times are outlined in Section 9.0.

7.3 For each analyte of interest, a blank and five standards will be used for calibration. Refer to Table 6.

7.4 Using injections of 25 µL of each calibration standard tabulate peak height or area response against the analyte concentration. The results are used to prepare a calibration curve for each analyte. The retention times are recorded and used to determine retention time windows for analyte identification. The width of the retention time window used to make identifications is based upon measurements of actual retention time variations of standards over the course of 72 hours. Three times the standard deviation of a retention time is used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

7.5 The calibration curve is verified on each working day, whenever the anion eluent is changed, and after every 10 samples. If the response or retention time for any analyte varies from the expected values by more than +/- 10%, the standard must be reanalyzed using fresh calibration mixes. If the results are still more than +/- 10%, a new calibration curve must be prepared for that analyte.

7.6 If a sample's analyte concentration exceeds the calibration range for that particular analyte, the sample must be diluted in so that the final concentrations fall within the calibration range No analytical results may be reported where sample concentration exceeds the concentration of the highest calibration standard for the analyte of interest.

8.0 Analytical Procedure

8.1 Refer to Section 11.0 of EPA Method 300.0.

8.2 Figure 2 below summarizes the mean estimated retention times for all analytes in this method derived from the current retention time window study and shall be used in the determination of the presence of a particular analyte

Figure 2 - Estimated Analyte Retention Times

Analyte	Mean Retention Time (min.)	SD
Bromide	5.94	0.05
Chloride	4.02	0.02
Fluoride	2.86	0.01
Nitrate	6.89	0.06
Nitrite	4.77	0.03
Ortho-Phosphate	9.07	0.05
Sulfate	10.54	0.08

8.3 A well mixed sample is loaded on the auto-sampler, flushing the 25 µL injection loop for 2 5 minutes after all system calibration criteria has been met.

8.4 The response for each analyte identified is used to calculate the sample concentration. If the response for the peak exceeds the working calibration range of the system, the sample must be diluted with deionized water and reanalyzed.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution identification

8.5 Soil Samples

8.6 The following extraction should be used for solid materials: Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed for ten minutes using a magnetic stirring device. The resulting slurry is filtered prior to injection using a 0.45 µm membrane filter. Analyze as in Section 9.3 above.

9.0 Calculations

9.1 Refer to Section 12.0 of EPA Method 300.0.and Section B.4 of the Dionex Peaknet Software Users Guide.

9.2 The Dionex Peaknet Software generates a calibration curve for each analyte. This laboratory exercises external standard quantitation procedures. The software plots instrument response verses analyte concentration. The sample concentration is computed by comparing sample response with the standard curve. All results are multiplied by any dilution factor.

The instrument calculates sample concentration by the following equations:

$$Ac = Function(Rc)$$

Where:

Ac	=	amount of the analyte in the calibration standard
Function	=	a form of the current calibration curve function
Rc	=	is the response of the analyte in the calibration standard

After the response factors for the components in the calibration standard have been determined, the sample can be injected and the response-corrected concentration of the components are calculated as:

$$Cs = Function\ (Rs) * \frac{Vc}{Vs} * Ds$$

Where

Cs	=	the concentration of the analyte in sample
Function	=	a form of the current calibration curve function
Rs	=	the response of the analyte in the sample
Vc	=	is the volume of standard injected (25 ul)
Vs	=	the sample volume injected from the Method or Schedule
Ds	=	the dilution factor from the Method or Schedule for the sample

9.3 Refer to the *PeakNet Software Manual, Section B, Quantitation Techniques* for details on calculating the slope and y-intercept for a linear curve fit.

9.4 All results reported must fall between the lowest and highest calibration standard. Samples exceeding the highest standard should be diluted and reanalyzed.

9.5 Report results in mg/L or mg/Kg.

10.0 Quality Control

10.1 Refer to *Section 9.0 of EPA Method 300.0.*

10.2 Document general quality control objectives, where applicable, to the test method and the manner in which they are implemented.

10.3 All quality control measures shall be assessed and evaluated on an on-going basis. Quality control acceptance criteria shall be applied and used as a tool to determine the validity of the data.

10.4 Refer to the Quality Manual for summary of overall QC procedures and evaluations to be employed. The QM will support overall reference method QC requirements.

10.5 The laboratory has documented procedures for the acceptance/rejection criteria as dictated by the reference method.

10.6 The quality control requirements for this procedure consist of an initial calibration verification, daily analysis of a reagent blank, daily calibration standard, laboratory control samples, matrix spike samples, and continuing calibration verification standards.

10.6.1 Initial Calibration Verification (ICV)/ Continuing Calibration Verification (CCV or DCS). For all determinations, an ICV and reagent blank are analyzed at the beginning of the shift, followed by CCVs and reagent blanks after every tenth sample. The ICV/CCV is defined as a mid-range check standard, obtained from a different vendor, (certified second source), with respect to the initial calibration standards. The ICV/CCV must be within +/- 10% of the stated value. If the calibration cannot be verified within these specified limits, sample analysis may not continue, and the source of the problem must be identified and corrected. All samples must be bracketed by an acceptable CCV. If a CCV fails the specified limits, all samples analyzed prior to the failing CCV must be reanalyzed.

10.6.2 Method Blank : Analyze at least one reagent blank with each analytical batch of samples (defined as 10 samples) or daily, whichever is more frequent. Data produced from this quality control sample is used to assess contamination from the laboratory environment. Values above the MDL indicate laboratory or reagent contamination and corrective action must be taken.

10.6.3 Laboratory Control Sample (LCS): Analyze at least one LCS with each analytical batch (defined as 10 samples) or daily, whichever is more frequent. The accuracy of this quality control sample is calculated as percent recovery. If the recovery of any analyte of interest falls outside the established control limits, that analyte is judged to be out of control, and the source of the problem should be identified and resolved prior to continuing analyses. These limits are determined using +/- 3SD (three times the standard deviation).

10.6.4 Current Quality Control Limits

This laboratory has uses the method default laboratory control limits. Refer to Table 7.

10.6.5 Matrix Spike and Matrix Spike Duplicate: A matrix spike and a matrix spike duplicate must be analyzed with each analytical sequence. Calculate the percent recoveries and monitor against the recoveries in section above. Note any matrix effects when applicable or when outliers are encountered. Refer to Table 7 for acceptable recoveries and RPD ranges.

11.0 Method Performance

11.1 Refer to Section *13.0 of EPA Method 300.0*

11.2 Linear Calibration Range - The linear calibration range must be determined initially and verified every six months or whenever a significant change in instrument response is observed. This linear calibration range typically consists of a minimum of a blank and three calibration standards For all analytes determined by this procedure, this laboratory will use a minimum five-point calibration to ensure linearity for all portions of the analyte curve.

11.3 Retention Time Window Studies –Refer to the QM.

12.0 Corrective Action for Outlier Conditions

12.1 Any non-conformance must be brought to the attention of the appropriate Section Supervisor. A Sample Casualty Report must be filled out with details regarding the non-conformance. All corrective actions must be approved and verified by follow-up by the Section Supervisor. The QA Officer or the Project Manager must be notified in those instances where the initiated corrective action does not correct the situation. This entire process should normally be completed within 72 hours.

12.2 Non-conformances and corrective actions are addressed in the Non-conformances and Corrective Action SOP. Refer to these documents for further details and instructions. For analytical outliers for this method, the following corrective measure may be taken. These may include, but not limited to:

- ❑ Reanalysis of the initial calibration standards
- ❑ Reanalysis of the Quality Control Sample
- ❑ Replacement of the guard column
- ❑ Replacement of the analytical column
- ❑ Cleaning of both the guard and analytical columns
- ❑ Preparation of fresh eluent
- ❑ Onsite visit from instrument manufacturer

The source of the problem must be identified and corrected prior to continuing with the analyses.

13.0 Preventative Maintenance

13.1 Method requirements may indicate the implementation of preventive maintenance as part of the overall regime for the procedure. In such case, it shall be included as part of the standard operating procedure. Likewise, the preventive maintenance procedure must be documented in the instrument maintenance logbook or applicable logs These logs will also be generated, maintained, archived and stored according to details listed in Section 16. Consult the instrument manual for details on maintenance of the ion chromatography system.

14.0 Data Reduction, Assessment and Validation

14.1 A system for the review, reduction and reporting of analytical data is detailed in Data Reduction and Review SOP

14.2 The ion chromatography system employed at this facility will generate a result based on the initial calibration curve upon which the sample and QC are compared, (i.e. external calibration)

15.0 Record Keeping, Tracking and Archiving

15.1 This facility will maintain all documents generated with a specific tracking number or unique identifier that will allow tracking and archiving. Refer to Document Control Procedure SOP for procedures All logs generated must be recorded in the Record Logbook for Tracking of Extraction, Maintenance and Run Log.

15.2 Each document/log generated will be assigned a unique Document Tracking, DT, number that is traceable to the date of issuance. Likewise, this identifier will assist in retracing it back into the Record Log and will indicate the box number assigned to store the document upon archiving. In support of these activities an electronic database is maintained documenting an index of archived documents.

Refer to the Document Control Procedures SOP.

16.0 Training and Training Validation

Employee training on documented procedures may be found in the Employee Training SOP. Demonstration of the employee's training in the specific procedures involved in this method may be found in the Training Documents Log This documentation includes all in-house and outside training received and include items such as proficiency testing and information on performance testing results. A Demonstration of Capability is on file for each analyst performing the test.

17.0 Data Validation

Refer to the Data Reduction and Review SOP.

18.0 Health and Safety

Refer to the Chemical Hygiene Plan and Laboratory Safety Plan SOPs.

19.0 Waste Disposal and Pollution Management

Refer to the Waste Management Plan SOP for waste disposal procedures.

20.0 References

- LMP's Definitions, Acronyms, Symbols and Abbreviations Policy
- EPA, Determination of Inorganic Anions by Ion Chromatography Revision 2.1, August 1993
- Solid Waste Manual, SW846 Update III, December 1996.
- U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements Version 1.0 2 NOV 98.
- Standard Methods for the Examination of Water and Wastewater, 18th Edition.
- EPA, Methods for Chemical Analysis of Water and Wastes, EPA –600/4-79-020, March 1983
- NELAC, Quality Systems, Revision 15, May 25, 2001.
- NELAC, Program Policy and Structure, Revision 13, June 29, 2000
- 40 CFR Part 136 Appendix A.
- EPA Guidance for Preparing Standard Operating Procedures (SOPs), EPA QA/G-6, EPA/240/B-01/004, March 2001
- USEPA 2185 – Good Automated Laboratory Practices
- USEPA 600/4-79-020, Methods for Chemical Analysis of Water and Wastes, March 1983.
- OSHA Laboratory Standard, 29 CFR 1910.1450
- OSHA Compliance Guide, Kirk H. Ray, 8th Edition.
- *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.
- Laboratory Safety in Practice. A Comprehensive Compliance Program and Safety Manual.
- *"Safety in Academic Chemistry Laboratories"*. American Chemical Society Publication, Committee on Chemical Safety.
- *"Carcinogens – Working with Carcinogens"*, Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.
- Dionex Peaknet Software Users Guide

21.0 Tables

Table 1 - Equipment, Instrumentation and Apparatus

Item Description	Manufacturer	Catalog/Part #
DX 500 Ion Chromatography System	Dionex	
Cd 20 Conductivity Detector	Dionex	
GP Gradient Pump	Dionex	
EO 1 Eluent Organizer	Dionex	
PeakNet Chromatography Datasystem	Dionex	
Anion Guard-IONPAC AG14 Guard Column (4 x 50 mm)	Dionex	046134
Anion Analytical Column-IONPAC AS14 Analytical Column (4 x 250 mm)	Dionex	
Anion Suppressor Device- ASRS II Anion Self-Regulating Suppressor	Dionex	
Graduated Mixing Cylinders –50 mL	Fisher	08-549-5D
5.0 NK mL Vial with cap	Dionex	038141
2 mL Disposable Pipette	Fisher	13-678-25C
Magnetic Stir Plate	Corning PC-353	
Teflon Stir Bars- Various Sizes		
Beakers, 150 mL	Fisher	02-540-J
Filtration Apparatus	Gelman	
0.45 µm Membrane Filters	Whatman	0990-210

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Table 2 - Certified Solutions

Standard ID	Vendor	Catalog #	Concentration
Sodium Carbonate	Dionex	037162	0.5 M
Sodium Bicarbonate	Dionex	037163	0.5 M
Fluoride	Crescent	CCS-803	5.0 mg/L
Bromide	Crescent	CCS-803	10 mg/L
Nitrite	Crescent	CCS-803	20 mg/L
Chloride	Crescent	CCS-803	40 mg/L
Nitrate	Crescent	CCS-803	40 mg/L
Phosphate	Crescent	CCS-803	40 mg/L
Sulfate	Crescent	CCS-803	50 mg/L
Sulfuric Acid, 0.02N	Fisher	SA226-4	0.02 N
Second Source:			
Fluoride	SCP Science	904-6E4-001	5.0 mg/L
Bromide	SCP Science	904-6E4-001	10 mg/L
Nitrite	SCP Science	904-6E4-001	20 mg/L
Chloride	SCP Science	904-6E4-001	40 mg/L
Nitrate	SCP Science	904-6E4-001	40 mg/L
Phosphate	SCP Science	904-6E4-001	40 mg/L
Sulfate	SCP Science	904-6E4-001	50 mg/L

Refer to Table 6 for the Initial Calibration dilution schedule.

Table 3 - Dilution Schedule Solutions

Solutions listed here are made as intermediate solutions to be used in the preparation of a working standard for instrument calibration/verification or for spiking solutions, which will be added directly to samples during preparation. All solutions are prepared in water unless otherwise noted.

Standard ID	Solution ID mg/L	Volume mL	Final Volume mL	Concentration mg/L
Fl- CCV (DCS)	Stock	25	50	2.50
Cl- CCV (DCS)	Stock	25	50	20.0
NO_2 CCV (DCS)	Stock	25	50	3.05
Br- CCV (DCS)	Stock	25	50	5.00
NO_3 CCV (DCS)	Stock	25	50	4.52
PO_4 CCV (DCS)	Stock	25	50	6.52
SO_4 CCV (DCS)	Stock	25	50	25.0
Eluent Solution	0.5 M Sodium Carbonate/0.5 M Sodium Bicarbonate	35.0/10.0	1000	
Fl-LCS/MS	Stock	25	50	2.50
Cl-LCS/MS	Stock	25	50	20.0
NO_2-LCS/MS	Stock	25	50	3.05
Br-LCS/MS	Stock	25	50	5.00
NO_3 LCS/MS	Stock	25	50	4.52
PO_4 LCS/MS	Stock	25	50	6.52
SO_4 LCS/MS	Stock	25	50	25.0

Note: These standards are from a different lot from the same provider as the stock solutions and are considered a second source.

Table 4 - Solution Spiking Levels

Standard ID	Solution ID	Volume mL	Final Volume mL	Final Concentration mg/L
Fl-LCS/MS	Stock	25	50	2.50
Cl-LCS/MS	Stock	25	50	20.0
NO_2-LCS/MS	Stock	25	50	3.05
Br-LCS/MS	Stock	25	50	5.00
NO_3 LCS/MS	Stock	25	50	4.52
PO_4 LCS/MS	Stock	25	50	6.52
SO_4 LCS/MS	Stock	25	50	25.0

Table 5 - Reagents/Solvents

Reagent	Grade	Manufacturer	Vendor/Cat #
Water	Type II	Inhouse	
Regeneration Solution, 0 02 N Sulfuric Acid	A C.S Grade	Fisher	SA226-4

Table 6 - Working Standards Dilution Schedule

Solution ID	Standard ID	Volume mL	Final Volume mL	Concentration mg/L
Br- Stock	Br-Cal 4	25	50	5
Br- Stock	Br-Cal 5	-	-	10
Cl-Stock	Cl-Cal 4	25	50	20
Cl-Stock	Cl-Cal 5	-	-	40
Fl- Stock	Fl-Cal 4	25	50	2.5
Fl- Stock	Fl-Cal 5	-	-	5
NO_2 Stock	NO_2 Cal 4	25	50	3.05
NO_2 Stock	NO_2 Cal 5	-	-	6.09
NO_3 Stock	NO_3 Cal 4	25	50	4.52
NO_3 Stock	NO_3 Cal 5	-	-	9.04
PO_4 Stock	PO_4 Cal 4	25	50	6.52
PO_4 Stock	PO_4 Cal 5	-	-	13
SO_4 Stock	SO_4 Cal 4	25	50	25
SO_4 Stock	SO_4 Cal 5	-	-	50
Stock	Br-Cal 1	2	200	0.1
Stock	Br-Cal 2	5	50	1
Stock	Br-Cal 3	25	100	2.5
Stock	Cl-Cal 1	2	200	0.4
Stock	Cl-Cal 2	5	50	4
Stock	Cl-Cal 3	25	100	10
Stock	Fl-Cal 1	2	200	0.05
Stock	Fl-Cal 2	5	50	0.5
Stock	Fl-Cal 3	25	100	1.25
Stock	NO_2 Cal 1	2	200	0 061
Stock	NO_2 Cal 2	5	50	0 61
Stock	NO_2 Cal 3	25	100	1.52
Stock	NO_3 Cal 1	2	200	0.09
Stock	NO_3 Cal 2	5	50	0.904
Stock	NO_3 Cal 3	25	100	2 26
Stock	PO_4 Cal 1	2	200	0.13
Stock	PO_4 Cal 2	5	50	1.3
Stock	PO_4 Cal 3	25	100	3.26
Stock	SO_4 Cal 1	2	200	0 5
Stock	SO_4 Cal 2	5	50	5
Stock	SO_4 Cal 3	25	100	12.5

Table 7 - Percent Recoveries & RPD's

Analyte	Ion	LCS % Rec.	MS/MSD % Rec.	MS/MSD RPD Range
Bromide	Br-	90-110	80-120	0-20
Chloride	Cl-	90-110	80-120	0-20
Fluoride	Fl-	90-110	80-120	0-20
Nitrite	NO_2	90-110	80-120	0-20
Nitrate	NO_3	90-110	80-120	0-20
Ortho-Phosphate	OP-	90-110	80-120	0-20
Sulfate	SO_4	90-110	80-120	0-20

Table 8- Detection Limits

Analyte	Aqueous MDL (mg/L)	Aqueous MQL (mg/L)
Bromide	0.078	0.200
Chloride	0.170	1.00
Fluoride	0.021	0.100
Nitrite	0.028	0.100
Nitrate	0.049	0.100
Ortho-Phosphate	0 111	0.200
Sulfate	0 253	1.00

Batch:_____
Date/Time Analyzed:_____ **Units:**_____ **Analyst** _____

ETC Sample ID	SS/DF*	F	Cl-	NO2	Br-	NO3	O-PO4	SO4
DCS								
BLK								
LCS								
LCS % Rec								
MS								
MSD								
MS/MSD%Rec								
BLK								
LCS								
LCS % Rec								
MS								
MSD								
MS/MSD%Rec								
BLK								
LCS								
LCS % Rec								
LCS Values mg/L:		2.50	25.0	4.57	5.00	4.52	6.52	25.0

Analyst:_____ **SS/DF*=** Sample Size/Dilution Factor **DCS SRN:**_____
Supervisor:_____ **Initial Calibration Date:**_____ **MS SRN:**_____
Amount of Spiking Solution:

Alkalinity by Titration

EPA 310.1

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

Alkalinity of water is its acid-neutralizing capacity. It is the sum of all bases that can be titrated. It is taken as a measurement of carbonate, bicarbonate and hydroxide concentrations.

2.0 Summary of Method

Samples are titrated with a standard sulfuric acid solution to an endpoint of pH 4.5. The endpoint is determined with the use of a pH meter.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts of interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and solvents may be necessary.

3.2 Glassware contamination can result in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem. Chromic acid that is not completely rinsed will cause similar problems with analyte degradation and should be carefully rinsed to avoid this problem. Refer to the SOP for cleaning of laboratory glassware.

3.3 The sample must not be filtered, diluted, concentrated, or altered in any way

4.0 Equipment and Apparatus

4.1 Jenco pH meter

4.2 Beakers of various sizes

4.3 Buret

4.4 Magnetic stirrer

4.5 Dropper

5.0 Reagents and Standards

5.1 Policy

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents/solvents/standards must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Program (SVQAP). This program is detailed in the Quality Manual.

5.2 Reagents

5.3 Solutions/Standards

Standard sulfuric acid solution, 0 02 N; (Ricca brand)

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

Refer to EPA 310.1 for guidance concerning containers, preservation and holding time.

6.2 Holding Times

6.2.1 Samples should be stored and refrigerated at 4oC

The sample should be run as soon as practical. Do not open the sample bottle before analysis.

7.0 Procedure

7.1 Alkalinities above 20 mg/L

7.1.1 Calibrate pH meter per manufacturer instructions. Rinse the electrodes with distilled water.

7.1.2 Transfer 100-ml sample into a 250-ml beaker and record the sample volume on the work sheet. The sample must be at room temperature prior to measurement.

7 1 3 Fill a buret with 0.02 N sulfuric acid and record the initial reading.

7.1.4 Stir with a magnetic stirrer being sure not to agitate the sample excessively and cause the loss of carbon dioxide.

7.1.5 Immerse the calibrated pH probe in the sample and continue stirring.

7 1.6 Slowly add, dropwise, the sulfuric acid until pH = 4 5.

7.1.7 Record the final reading of the buret.

7.2 Alkalinities below 20 mg/L

For alkalinities less than 20 mg/L titrate 200 ml according to Procedure A using 0.02N Standard Acid Solution Stop the titration at a pH in the range of 4.3 to 4.7 and record the volume and exact pH. Add additional titrant to reduce the pH exactly 0.30 pH and again record volume.

8.0 Quality Control/Quality Assurance/Corrective Action

8.1 Duplicate analyses will be performed on a daily basis or at a minimum of every 10 samples, whichever is more frequent

8 2 Control limits are available and will be recorded on the QC sheet If any quality control data fall outside the QC limits, the analyst MUST notify the supervisor IMMEDIATELY. All deviations MUST be noted on the QC data sheet as well as corrective actions. The QC Officer MUST be notified of all infractions.

8 3 Corrective Action - Corrective Action is the process by which problems within the laboratory are identified, proper personnel are notified, the problem solved or justified, correction implemented and the Corrective Action documented.

9.0 Calculations

9.1 Calculation for Alkalinities above 20 mg/L:

$$\text{Alkalinity as calcium carbonate (mg/L)} = \frac{A * B * 50000}{C}$$

Where:
A = ml sulfuric acid titrant
B = normality of sulfuric acid
C = ml sample size

9.2 Calculation for Alkalinities below 20 mg/L:

$$\text{Alkalinity as calcium carbonate (mg/L)} = \frac{(2A - B) * N * 50000}{C}$$

Where:
A = ml titrant to first recorded pH
B = ml titrant to reach pH 0.3 units lowers
N = Normality of sulfuric acid
C = mL sample

10.0 Data Validation

Refer to the Laboratory Quality Manual.

11.0 Waste Disposal

Consult the Waste Management Plan.

12.0 Health and Safety

See the Chemical Hygiene and Laboratory Safety Plans.

13.0 Training & Training Validation

See the Laboratory Employee Training SOP.

14.0 References

14.1 *"Carcinogens – Working with Carcinogens"*, Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

14.2 "OSHA Safety and Health Standards, General Industry", 29 CFR 1910.

14.3 *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.

14.4 *"Safety in Academic Chemistry Laboratories"*, American Chemical Society Publication, Committee on Chemical Safety.

14.5 Standard Methods, 18th Edition, Method 2320B.

14.6 Methods for the Chemical Analysis of Water and Wastes, EPA-800/4-79-020, March 1983, Method 310.1.

14.7 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements, Appendix H.

15.0 Appendix

Determination of Sulfide by

EPA Method 376.2

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

This method is used to indicate the presence of free sulfide ion, S^{2-}, dissolved hydrogen sulfide or as metallic sulfides commonly found in sewage and industrial wastewaters.

2.0 Summary of Method

The sulfide test is based on the ability of hydrogen sulfide and acid-soluble metallic sulfides to convert n,n-dimethyl-p-phenylenediamine oxalate directly to methylene blue. The intensity of the blue color developed is directly proportional to the amount of sulfide present in the original to the amount of sulfide present in the original sample.The amount of methylene blue is measured spectrophotometrically.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts of interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and solvents may be necessary.

3 1.1 Glassware contamination can result in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem. Chromic acid that is not completely rinsed will cause similar problems with analyte degradation and should be carefully rinsed to avoid this problem. Refer to the SOP for cleaning of laboratory glassware: Sigcln03.doc.

4.0 Equipment and Apparatus

4.1 Equipment

4.1.1 25 mL graduated cylinders

4.1.2 1 mL calibrated droppers

4.1.3 Spectronic 20 spectrophotometer

5.0 Reagents and Standards

5.1 Policy

5.1.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents/solvents/standards must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

5.1.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Program (SVQAP). This program is detailed in the Quality Manual

5 2 Reagents

5.2.1 HACH Sulfide 1 reagent

5.2.2 HACH Sulfide 2 reagent

5.2.3 Deionized water

5.3 Solutions/Standards

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

6.1.1 Refer to EPA Method 376.2 for details.

6.2 Holding Times

6.2.1 Holding Time for extraction is defined as the number of days from ***Sample Collection*** (e.g. Sample Date) to extraction.

6.2.2 Holding time for this procedure is 7 days. The sample is preserved with NaOH to a pH greater than nine and maintained at a temperature of 4°C.

7.0 Procedure

7.1 If samples are clear DI-water may be utilized to zero the spectrophotometer.

7.2 Take a sample of DI-water and place in cell holder of spectrophotometer whose wavelength has been adjusted to 670 nm. If samples exhibit varied turbidity, an original untreated sample will be used to zero the spectrophotometer.

7.3 Place enough of the original sample in the cell holder and again adjust to 670 nm. Adjust the instrument to zero absorbance.

7.4 Take a water sample and fill a 25 mL mixing cylinder with 25 mL of sample or a smaller aliquot diluted to 25 mL.

7.5 Using the 1 mL calibrated dropper add 1 mL of sulfide 1 reagent to the graduated cylinder, stopper and invert slowly to mix.

7.6 Using the 1 mL calibrated dropper add 1 mL of sulfide 2 reagent to the graduated cylinder, stopper, and invert slowly to mix. A blue color develops if sulfides are present; a pink color indicates no sulfides. Allow 5 minutes for the color to fully develop before taking the reading. Place in cell holder and record the absorbance on the worksheet. Refer to sulfide concentration chart to determine actual sulfide concentration.

8.0 Quality Control/Quality Assurance

8.1 A duplicate, blank and LCS must be run on a daily basis or at a minimum of one every 10 samples.

8.2 The worksheet must be completed, initialed, and dated.

8.3 Control limits will be available and the analyst and supervisor should have these limits on hand. These limits will be recorded on the QC data sheet. The data should fall within the upper and lower control limits. Should the QC data fall outside the QC limits the analyst must notify their supervisor immediately. Note all deviations on the QC data sheet as well as corrective measures. The QA Officer should be notified of all infractions.

9.0 Calculations

Not applicable.

10.0 Data Validation

Refer to the Laboratory Quality Manual.

11.0 Waste Management

Refer to the Waste Management Plan.

12.0 Health and Safety

Consult the Chemical Hygiene and Laboratory Safety Plans.

13.0 Training & Training Validation

Refer to the Employee Training SOP and QM.

14.0 References

14.1 *"Carcinogens – Working with Carcinogens"*, Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

14.2 "OSHA Safety and Health Standards, General Industry", 29 CFR 1910.

14.3 *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.

14.4 *"Safety in Academic Chemistry Laboratories"*, American Chemical Society Publication, Committee on Chemical Safety.

14.5 Standard Methods, 18th Edition.

14.6 Code of Federal Regulations 40 CFR Part 136.

14.7 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements, Appendix H.

14.8 EPA Methods for Chemical Analysis of Water and Wastes, EPA 600\4-79-020.

15.0 Appendix

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TCLP Extraction by Method 1311

And SPLP by Method 1312

Prepared by: _____
Michael Kauffman. Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

1.1 This SOP describes the preparation of samples for organic and inorganic analysis by EPA Method 1311, the Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP). TCLP/SPLP extraction is used to determine the mobility of analytes in an acetic acid buffer solution.

1.2 Sample/Reagent Handling Cautions

1.2.1 The solvents and reagents used in this extraction procedure are hazardous if improperly handled. Care must be taken during preparation and use of the acetic acid, hydrochloric acid, nitric acid, and sodium hydroxide solutions.

1.2.2 The acetic acid extraction fluid in the nonvolatile extraction vessels may react with carbonates in the sample to form CO2 gas. Pressure buildup could potentially cause the vessels to explode. The vessels should be periodically vented during the extraction, and once again prior to removal from the rotation apparatus to prevent this occurrence.

1.2.3 Proper precautions must be taken when using pressurized nitrogen during the filtration and pressurization procedures.

2.0 Summary of Method

2.1 The wastes are initially characterized and defined by matrix (liquid, solid, or mixed phase) and by pH. This preliminary characterization determines the type of TCLP extraction procedure to be applied. Wastes containing less than 0.5 percent dry solid material are classified as liquid wastes and, after filtration, are defined as the final TCLP extract. If the wastes contain greater than or equal to 0.5 percent solids, the liquid, if any, is separated from the solid phase and stored for later analysis. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. Samples for volatiles analysis are extracted in a special pressurized extraction vessel Extractions are conducted for a period of 18 hours, followed by analysis of the extract by approved EPA methodology.

This method is applicable to liquid, solid, and multiphasic wastes TCLP extractions need not be performed for those samples shown, by previous analysis, to contain levels of analytes that could not possibly exceed the TCLP regulatory limits. If any regulated compound in an extract exceeds the regulatory limits, the waste is determined to be hazardous. The remaining TCLP fractions need not be analyzed.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by the extraction and analysis of method blanks. Specific selection of reagents and solvents may be necessary.

3.2 Refer to method specific SOPs for additional details related to the particular fraction (e.g. metals, BNAs, VOCs...).

3.3 Method blanks must be extracted with each preparation batch to demonstrate that the system is free from method interferences.

High purity reagents must be used to minimize interference problems.

4.0 Equipment and Apparatus

4.1 Rotary Agitation Apparatus - Five-port, capable of end-over-end rotation at 30 ± 2 rpm. Environmental Express Model, or equivalent.

4.2 Extraction Vessels

4.2.1 Zero-Headspace Extraction Vessel (ZHE) - Internal volume of 500-600 mL, and equipped to accommodate a 90-110 mm filter.

4.2.2 O-rings, top and bottom flange, Associated

4.2.3 Bottle Extraction Vessel - Borosilicate medium walled glass, Teflon screw cap, 2.5 L volume. Plastic 1 gallon HDPE container.

4.3 Filtration Apparatus - Stainless steel

4.4 Filtration Apparatus – Buchner funnel with vacuum

4 5 ZHE Extraction Fluid Transfer Device – 60-ml HDPE gastight syringe with Teflon stock-cock valve.

4.6 pH Meter – Corning 320

4.7 Laboratory Balance – Top Loading Ohaus GT4100 (or equivalent) capable of weighing +/- 0.01 grams.

4.8 Magnetic stirrer

4.9 Thermometer – Monitor TCLP extraction room temperature. Temperature should be 23°C +/- 2°C

4.10 Glassware and Miscellaneous Supplies

4.10.1 Beakers, glass, 250-, 500-, 1000-, and 2000-mL

4.10.2 Graduated cylinders, glass, 100- and 2000-mL.

4.10.3 Erlenmeyer flasks, glass, 1000-mL.

4.10.4 Watch glasses

4.10 5 Glass Microfiber Filters – CPI

4.10.6 Acid wash filters used to prepare inorganic samples for TCLP extraction by rinsing with 1N nitric acid. Follow by carefully rinsing the filters several times with deionized water.

4.11 Compressed nitrogen

4.11.1 Single stage pressure regulator

4.11.2 Flexible tubing capable of withstanding pressures up to 100 psi, with a quick disconnect attachment.

5.0 Reagents and Standards

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Procedure (SVQAP).

5.3 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One of SW846

5.4 Glacial acetic acid, ACS reagent grade.

5.5 Hydrochloric acid (1N), ACS reagent grade. Add 83 mls of concentrated (1 +11) hydrochloric acid to 1000mls of water. **Always add acid to water.**

5.6 Sodium hydroxide (10N), ACS reagent grade. Weigh 400g of NaOH to 1000mls of water. Stir until dissolved. **Caution: This procedure generates heat!**

5.7 Nitric acid (1N), ACS reagent grade. Add 64mls of concentrated nitric acid per 1000mls of water. **Always add acid to water.**

5.8 Extraction fluid #1, pH = 4.93

5.9 Extraction fluid #2, pH = 2.88

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

6.1.1 Refer to the Quality Manual for guidance concerning containers, preservation and holding times.

6.2 Holding Times

6.2.1 Holding time for extraction is defined as the number of days from ***sample collection*** (e.g. sample date) to extraction.

6.2.2 Holding time for analysis is defined as the number of days from ***sample extraction*** in the laboratory to date injected/analyzed by the instrument.

NOTE: For volatiles (GC or GC/MS, low level or medium level) holding time is always defined as the number of days from ***sample collection*** until analysis.

6.2.3 Preservation should not be added to samples before leaching.

6.2.4 TCLP extractions and the analysis of the extracts must be conducted within the time periods specified in this SOP or other referenced documents. However, analysis of the extracts should be conducted as soon as possible after the TCLP extraction Extracts to be analyzed for metals must be preserved with nitric acid to a pH of less than 2, unless precipitation occurs. If precipitation is observed, follow he steps outlined in the following section.

6.2.5 TCLP extractions, preparations, and analyses must be conducted within the following time periods:

6.2.5.1 From Field Collection to TCLP Extraction Volatiles 14 days, Semivolatiles 14 days Mercury 28 days, Metals, except mercury 180 days.

6.2.5.2 From TCLP Extraction to Preparation Extraction, Volatiles Not Applicable Semivolatiles 7 days, Mercury Not Applicable, Metals, except mercury Not Applicable.

6.2.5.3 From Preparation Extraction to Analysis Volatiles 14 days, Semivolatiles 40 days, Mercury 28 days, Metals, except mercury 180 days.

Total Elapsed Time Volatiles 28 days, Semivolatiles 61 days, Mercury 56 days, Metals, except mercury 360 days

7.0 Procedure

The TCLP preparation procedure can be broken down into four steps:

- Preliminary Sample Evaluation
- Preparation of Extraction Fluids
- TCLP Extraction Procedure for Nonvolatile Analytes
- TCLP Extraction Procedure for Volatile Compounds

7 1 Preliminary Sample Evaluation

A preliminary evaluation of the samples is performed prior to TCLP extraction. The results of the evaluation determine how the extraction is conducted and how the results are reported. The preliminary evaluation includes the following:

- Determination of percent solids
- Determination if the waste contains insignificant amount of solid material, and is therefore the TCLP extract after filtration.
- Determination if the solid part of the waste needs particle size reduction.
- Determination of the extraction fluid to be used for the nonvolatile extractions, based on the pH of the waste.
- Examine the samples. If the samples contain no obvious liquid phase, and contain pieces of material that exceed 1 cm in diameter, proceed to Section 7.1 2 for particle size reduction before continuing.

7.1.1 Percent Solids Determination - The samples are filtered under pressure through glass microfiber filters. The percentage of total sample from which liquid cannot be forced out is defined as the percent solids.

7.1.1.1 Prior to assembly of the filtration apparatus, clean all parts by washing with soapy water followed by rinsing with deionized water and reagent grade water.

7.1.1.2 Weigh a Whatman glass microfiber filter (grade GF/F, 14.2 cm diameter) and record the weight on the TCLP preparation worksheet.

7.1.1.3 Rinse the glass filter paper and the metal filter screen with reagent grade water. Place the filter paper on the screen and in the extractor such that the glass fiber filter will be facing the sample.

7.1 1 4 Attach the bottom flange (the flange without the nitrogen quick disconnect attachment).

7.1 1.5 Turn the apparatus so that it is right side up. Weigh a 250-mL beaker, record the weight on the worksheet.

7.1.1.6 Transfer 100 g (to the nearest 0.1 g) of a representative sub-sample of the waste into a tarred 250 mL beaker. Record the total weight of the waste on the worksheet.

7 1 1.7 Carefully pour or spread the sample onto the filter paper in the cylinder. Material may stick to the sides of the beaker. Quantitatively determine the amount

transferred to the filtration apparatus by weighing the empty beaker, and record the weight on the worksheet.

Note: If the sample is a mixed phase sample, first decant and filter the liquid portion. After the liquid has been filtered, transfer the solid material onto the same filter and repeat the filtering process. If the sample consists of pure oil or solvent, consult the organics or inorganics supervisor before proceeding. Oils are usually treated as solids (oils may or may not be filterable).

7.1.1.8 Attach the top flange.

7.1.1.9 Attach the nitrogen line to the connector on the top flange.

7.1.1.10 Slowly apply pressure.

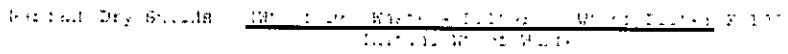
7.1.1.11 Apply pressure in 10 psi increments. Hold at each step for 2 minutes after liquid stops coming out. Do not pressurize the apparatus beyond 50 psi

7.1.1 12 If no liquid is forced from the sample, the sample is considered to be 100% solid waste. Proceed to Section 7.1.3.

7.1.1.13 Open the filtration apparatus.

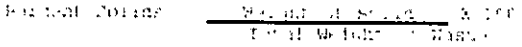
7.1.1.14 If it is obvious by looking at the material on the filter that a significant amount (more than 0.5%) of the material is solid, go to the appropriate section below.

7.1.1.15 If a small amount of residue remains on the filter, carefully remove the filter and dry it at 100 ± 2 o C for one hour. Weigh the filter and waste and record the weight on the TCLP worksheet. Return the filter to the oven for an additional 15 minutes and reweigh it to demonstrate that constant weight has been reached. Use the following calculation to determine the Percent Dry Solids:



7.1.1.16 If the percent dry solids exceed 0.5%, go to the appropriate section below. If the percent dry solids are less than 0.5%, the filtrate becomes the TCLP extract. Additional sample may need to be filtered to meet the volume required for analysis. After sufficient sample has been filtered, proceed to Section 7.3 3.

7.1.1.17 Weigh the beaker and the filtrate, record on the worksheet, and subtract the initial beaker weight. The filtrate is the liquid phase. The initial sample weight minus the weight of the liquid phase is the solid phase weight A percent solid is calculated as follows:



7.1.1 18 If the percent solid exceeds 0 5%, the liquid, if any, is saved for either future combination with the TCLP extract or for separate analysis.

7.1.2 Particle Size Reduction

The solid portion (0.5% solids) of the samples are evaluated to determine whether particle size reduction is needed.

7.1.2.1 If the solid material in the sample can pass through a 9.5 mm sieve (less than 1 cm in diameter), particle size reduction is unnecessary.

7.1.2.2 If the samples need particle size reduction, crush or grind the sample with a mortar and pestle prior to extraction.

7.1.2.3 Note the particle size reduction on the TCLP worksheet. After particle size reduction is complete, return to Section 7.1.1.

7.1 3 pH Analysis to Determine Extraction Fluid Type For Non-volatile Analyses. An aliquot of the sample is initially tested for pH. The results determine which fluid is used for the nonvolatile TCLP extraction. **Volatiles TCLP extraction uses only extraction fluid #1.**

7.1.3.1 Weigh out 5.0 g of the solid phase of the sample into a tarred 250-mL beaker Note: pH is determined after particle size reduction described in Section 7.1.2.

7.1.3 2 Add 96.5 mL of reagent water to the beaker, cover with a watch glass, and stir with a magnetic stirrer for 5 minutes.

7 1 3 3 Using a pH meter, measure the pH of the sample and record it in the TCLP sample preparation logbook

7.1.3.4 If the pH is less than 5, use extraction fluid #1 for the TCLP sample extraction.

7.1.3.5 If the pH is greater than 5, with a 10 mL disposable pipette, add 3 5 mL of 1N HCl, slurry briefly, and cover with a watch glass. Warm the slurry to 50 o C on a hotplate and hold at that temperature for 10 minutes.

7.1.3.6 Allow the solution to cool to room temperature, measure the pH, and record the result on the worksheet.

7 1.3.7 If the pH is now less than 5, use extraction fluid #1 as the sample extraction fluid. If the pH is still greater than 5, use extraction fluid #2.

7.1.3.8 Record the extraction fluid used for each sample on the TCLP extraction worksheet.

7 2 Preparing Extraction Fluids

One of two TCLP extraction fluids are used for the nonvolatile extractions, with the sample pH as the determining factor. Extraction fluid #1 is the only fluid used for volatile TCLP extractions and is the most commonly used. Percent solids and pH analyses must be performed prior to preparation of the extraction fluid(s). The sample extraction fluids should not be stored for more than 48 hours. If the extraction fluid is made more than 24 hours before use, the pH must be checked prior to extraction.

7.2.1 Preparation of Extraction Fluid # 1 (pH 4.93 ± 0 05).

7.2.1.1 Add reagent water to mixing container.

7.2.1.2 Add 11 4mL of glacial acetic acid per 1000mls of reagent water. Record the lot number and volume in the logbook.

7.2.1.3 Add 6.43mL of 10 N NaOH per 1000mls of reagent water. Record the lot number and volume in the logbook

7.2.1.4 Using the pH meter, monitor the pH of the solution. Stir with a magnetic stirrer until the pH stabilizes.

7.2.1.5 If the pH is too high, adjust by slowly adding glacial acetic acid to the extraction fluid to bring the pH down to 4.93 ± 0.05.

7.2.1.6 If the pH is too low, adjust by slowly adding 10 N NaOH to the extraction fluid to bring the pH up to 4.93 ± 0.05. Record the total volume and pH in the logbook.

7.2.2 Preparation of Extraction Fluid # 2 (pH 2.88 ± 0.05).

7.2.2.1 Add 11.4mL of glacial acetic acid per 1000mls reagent water. Record the lot number and volume in the logbook.

7.2.2.2 If necessary, adjust the final extraction fluid pH by adding only glacial acetic acid or water. Do not use the sodium hydroxide solution.

7.2.2.3 Record the total volume and pH in the logbook.

7.3 TCLP Extraction Procedure - Nonvolatile Samples

This procedure describes the TCLP extraction of samples for semivolatile, pesticide, and metal analysis. Preliminary sample evaluations must be completed before the TCLP extractions are performed. If only one sample has been received for volatile, semivolatile, pesticide, and metal TCLP analysis, the volatile TCLP extraction must take place first (Section 7.4) This limits the loss of volatile analytes and helps prevent volatile sample contamination.

7.3.1 Glassware Preparation

All extraction vessels, glassware and utensils used for the extraction procedure must be washed with soapy water and rinsed with tap water and reagent grade water (ASTM Type II).

7.3.2 Extraction Vessel Blanks

The nonvolatile extraction vessels are 2-liter borosilicate glass bottles with teflon screw caps or fluorinated wide-mouth plastic bottles. Each extraction vessel must be demonstrated to be free of contamination by performing a blank extraction in every vessel prior to sample extraction. Blanks are required after 20 TCLP extractions have been performed on a particular vessel. At least one blank must be extracted per SDG per extraction fluid. A separate blank is required for ZHE for each SDG.

7.3.3 Liquid Phase Samples

If the samples have been found to contain less than 0.5% dry solids, the filtrate is the TCLP extract (Section 7.1.1.18) Sample in addition to that used in the preliminary evaluation may need to be filtered to provide sufficient volume for all the requested analyses

7.3.3.1 Set up the filtration apparatus as in Section 7.1.1 and follow the filtration procedure as described. It is unnecessary to weigh and record the filter weight.

7.3.3.2 If metals are to be analyzed, acid wash the filter prior to filtration.

7.3.3.3 Collect the filtrate in a 1-L Erlenmeyer flask.

7.3.3.4 If the filtrate is to be analyzed for metals, adjust the pH to less than 2 with 1N nitric acid. Check an aliquot for precipitation before acidifying the entire extract. If a precipitate does form, do not adjust the pH of the extract.

7.3.4 Solid Phase Samples

If the sample is found to be 100% solids, and requires no particle size reduction, Tare a 250 mL beaker; weigh out a 100.0 g aliquot. Quantitatively transfer the aliquot to the extraction vessel and record the vessel number. Record the weight of the empty beaker in the TCLP extraction logbook and determine sample weight by subtraction.

7.3.4.1 If required, perform particle size reduction as in Section 7.1.2 before continuing.

7.3.4.2 Weigh into an extraction vessel a duplicate aliquot for the sample designated as the QC sample. An additional aliquot may also be needed to obtain sufficient TCLP extract volume matrix spike analyses. In either instance, repeat the instructions given in Section 7.3.4.

Note: The matrix spiking solution for any analysis (Semivolatiles, pesticides, or metals) must not be added to the extraction fluid prior to TCLP extraction.

7 3.4.3 The volume of extraction fluid used is 20 times the sample weight For example, with a 100 g sample aliquot, use 2000 mL of extraction fluid.

7.3.4.4 After the sample has been added to the extraction vessel, add the appropriate amount of extraction fluid to the vessel. Extraction fluid volume is 20 times the weight of the solid phase. For example, sample weight of 95 g requires 1900 mL of extraction fluid. Record the volume of extraction fluid on the worksheet.

7.3.4.5 Cap the vessel. Write the sample number on the vessel with a marking pen.

7.3.4.6 Rotate the vessels at 30 ± 2 rpm for 18 ± 2 hours. Record the analyst, date, time and temperature at the beginning and end of the extraction. The temperature in the room should be maintained at 22 + 3 o C.

Note. For some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide), pressure may build up within the extractor bottle during extraction To relieve excess pressure, periodically vent the extractor bottle into a hood. Venting after 15 minutes, 30 minutes, and every ½ hour until pressure build up is no longer occurring is usually sufficient, but the analyst must exercise their judgement based on observation of the sample.

7.3.4.7 When the extractions are complete, remove the extractors from the rotator and separate the liquid and solid phases by filtering through a new glass fiber filter as outlined in Section 7 1.1.

7.3.4.8 Carefully decant the extraction fluid into the filtration apparatus and filter as described in Section 7.1.1. Do not record filter or filtrate weights. Collect the fluid in appropriate containers, depending upon the requested analyses. Discard the solid material left in the vessel.

7.3.4.9 Measure and record the pH of the final extract.

7.3.4.10 If metals are to be analyzed, the filter must be acid washed and the pH of the extract corrected to < 2 with 1N nitric acid.

7.3.5 Mixed Phase Samples

If the samples are mixed phase, decant and filter the liquid part first as described in Section 7 1 1, using sufficient sample to perform the required analyses.

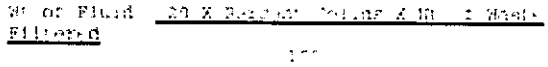
Note: If the samples are mostly liquid, a liter or more of the liquid may need to be filtered to accompany the requested analyses. If the majority of the sample is solid material, an aliquot of about 200 g should be sufficient. The QC sample requires larger aliquots.

7.3.5.1 After the liquid part of the aliquot has been filtered, pour or spread the solid material onto the same filter. Complete the filtration procedure, and record the weights of the filtrate and the solid material

7.3.5.2 Hold the liquid portion for future analysis, or for combination with the TCLP extract

7.3.5.3 Evaluate the solid portion of the sample and transfer to the extraction vessel following the instructions as indicated above.

7.3.5.4 When transferring the solid material in the filtration apparatus to the extraction vessel, include the filter. Record all weights in the TCLP preparation logbook. Use the following calculation to determine the amount of extraction fluid to use:

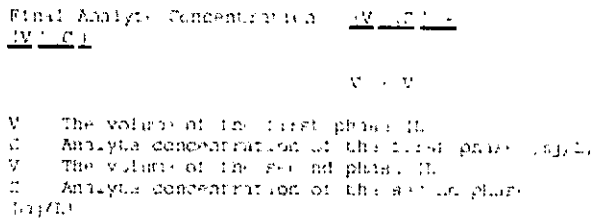


7.3.5.5 Conduct the extraction of the solid material.

7.3 5.6 If the filtered liquid phase of the mixed phase sample is compatible with the liquid extract from the solid phase extraction, combine the phases. This combination is the final mixed phase TCLP extract. Indicate on the TCLP worksheet as Combined.

7.3.5.7 If the filtered liquid phase of the mixed phase sample is not compatible with the liquid extract, do not combine the phases.

7.3.5.8 The liquids are analyzed separately, and the results mathematically combined The following equation is used to obtain the final analyte concentrations:



7.3.5.9 Analyze the TCLP extracts according to the appropriate analytical methods.

7.4 TCLP Extraction Procedure - Volatile Samples

This method is used for the TCLP extraction of samples for volatile analytes. Care must be taken to minimize the loss of volatiles by limiting the exposure of the samples, the filtrate, and the extracts to the atmosphere. Headspace should not be allowed in any of the extraction or collection containers.

7.4.1 If the samples have been found to contain less than 0.5 percent dry solids, the filtrate is the TCLP extract (Section 7.1.1.18). Sample in addition to that used in the initial evaluation may need to be filtered to provide sufficient volume for all the requested analyses. If additional sample is needed, proceed as follows.

7.4.1.1 Set up the filtration apparatus and follow the filtration procedure as described. It is unnecessary to weigh and record filter weights.

7.4.1.2 Collect the filtrate directly into 60ml gastight syringes with stopcock valves, allowing no headspace.

7.4.1.3 Store the vials in the VOC lab refrigerator until analyzed.

7.4.2 Zero Headspace Extractors (ZHE) are used as the extraction vessels for solid material from which volatile analytes are to be analyzed. The ZHE has an internal capacity of 500 mL. Therefore, because of the 20 fold ratio of extraction fluid to sample, the maximum volatile sample size is 25 g.

7.4.3 Cleaning and Maintaining the ZHEs.

7.4.3 1 The ZHEs are stored completely disassembled.

7.4.3.2 Before the ZHEs are assembled, wash all the parts with hot, soapy water followed by rinsing with tap, deionized, and reagent grade water. Set the parts aside to dry. Make sure the pistons do not get interchanged

7 4 3 3 ZHE O-rings must be free of cracks or cuts, or the extractors may leak. Before assembly, examine the O-rings for damage. Keep a stock of replacement O-rings available.

7.4.4 ZHE Assembly

7.4.4.1 To assemble the ZHE, place the cylinder on the ZHE support chair.

7.4.4 2 Wet the cylinder with reagent grade water and place the piston in the cylinder.

7 4 4.3 Carefully align the piston with the cylinder so that it is level

7 4.4.4 Using the palm of your hand, slide the piston into the cylinder.

7.4.4.5 Place a Teflon rod in the center of the piston and use a rubber mallet to push the piston to ½ to ¾ inch below the surface of the cylinder.

7.4.4 6 If the piston does not move easily. the piston is not properly aligned with the cylinder. If so, remove the piston by inverting the apparatus and apply a minimal amount of force to the center of the piston with the Teflon rod. Do not force the piston or damage to the piston and cylinder will occur.

7 4.4.7 Once the piston is in place, invert the cylinder

7.4.4.8 With reagent water, wet the grooves and wipe with a cotton swab before placing the O-ring inside.

7.4.4.9 Place the O-ring(s) in the groove and re-wet to insure a good seal

7.4.4.10 Place the bottom flange with the pressure gauge on the cylinder and secure the knobs.

7.4.4.11 Invert the cylinder.

7.4.4.12 Rinse the 2 filter screens and a Whatman glass microfiber filter (grade GF/F, 9.0 cm diameter) with reagent grade water.

7.4.4.13 Place the glass fiber filter between the 2 filter screens. Place the filters on top of the O-ring and assemble the top flange.

7.4.5 Leak-testing the ZHE

7.4.5.1 Pressurize the ZHE to 50 psi and place in a large container of water. If bubbles escape from the vessel, the seals are leaking.

7.4.5.2 7.4.5.2 De-pressurize the ZHE and open the side that is leaking and re-wet the O-rings. Recheck for leaks in the seal.

7.4.6 Transfer of Sample to the ZHE

7.4.6.1 Once the ZHE is determined to be leak free, remove the top flange.

7.4.6.2 Blanks - As in Section 7.3.2, vessel blanks are conducted before each TCLP extraction project and after 20 extractions have been performed on each vessel.

7.4.6.3 Bolt on the top flange and load 500 mL of extraction fluid into the vessel as described in this SOP.

7.4.6.4 Pressurize, rotate, remove, and store the blank extracts as described in Sections 7.4.7 and 7.4.8.

7.4.6.5 If the sample matrix is 100% solid material, and particle size reduction is unnecessary, weigh 25 g of sample to the nearest 0.1 g. If the sample matrix is mixed phases proceed to Section 7.4.6.6.

7.4.6.6 Quickly transfer the sample to the ZHE and attach the top flange.

7.4.6.7 If particle size reduction is needed, proceed as in Section 7.1.2 before continuing. Record the sample weight on the TCLP worksheet. Go to Section 7.4.6.16.

7.4.6.8 If the sample matrix is a mixed phase, use the percent solids information from Section 7.1.1 and the following calculation to determine the correct sample size to use:

$$\text{Wt. of Waste to Charge ZHE} = \frac{25}{\text{Percent Solids}} \times 100$$

7.4.6.9 Pour the appropriate weight of the mixed waste slurry into a tarred beaker and transfer to the ZHE, quickly attaching the top flange.

7.4.6.10 Reweigh the beaker and record the weight on the TCLP worksheet.

7.4.6.11 Attach the pressurized nitrogen source to the ZHE.

7.4.6.12 Attach a luer lock syringe to the valve at the top of the ZHE to collect the liquid fraction.

7.4.6.13 Pressurize the ZHE to 10 psi and slowly open the luer lock valve.

7.4.6 14 Increase the pressure in increments of 10 psi every 2 minutes, until no more liquid is forced from the sample Do not pressurize the ZHE more than 50 psi. Discard the first 5 mL of liquid collected.

7.4.6.15 Store the liquid fraction in a VOA vial at 4 o C for either combination with the TCLP extract or independent analysis.

7.4.6.16 Disconnect the nitrogen line and release the pressure on the piston by opening the release valve on the bottom flange of the ZHE.

7.4.6.17 Leave the release valve open while injecting the fluid.

7.4 6.18 Use the following formula to determine how much extraction fluid #1 to add to the ZHE:

$$\text{mL Extraction Fluid \#1} = \frac{20 \times \text{Percent Solids} \times \text{Wt. of Waste Filtered}}{100}$$

For example, if the sample has been classified as 100% solid, 500 mL of extraction fluid will have to be injected.

7.4 6 19 Connect the nitrogen line to the quick disconnect attachment and slowly pressurize the ZHE to 10 psi.

7 4 6.20 Rotate the vessel end over end several times. Partially open the inlet/outlet valve to ensure no headspace exists in the ZHE. Close the valve immediately when the fluid starts to come out.

7.4.7 Rotary Agitation

7.4.7.1 Bolt the ZHEs in the rotary agitation apparatus and rotate at 30 ± 2 rpm for 18 ± 2 hours. Record the analyst, date, time and temperature at the beginning and end of the extraction. The temperature in the room should be maintained at 22 + 3 o C.

7.4.7.2 When rotation is complete, check that the pressure gauges still read 10 psi. If the vessel is no longer pressurized, repeat the extraction with a new sample.

7 4.8 Removal of the Extract from the ZHE

7.4.8.1 Once the contents of the ZHE have settled, attach the extraction fluid syringe to the inlet/outlet valve.

7.4.8.2 Slowly open the inlet/outlet valve and allow the fluid to enter the syringe. Remove no more than 450 mL of the fluid to ensure that the solid material will not be forced into the steel filter screens.

7 4.8.3 Cap the syringe with a luer-lock valve (closed) Transfer to the VOC refrigerator.

7.4.8.4 If there is no initial liquid phase, collect and store the extract as in section 7.4.8.3.

7.4.8.5 If a separate initial phase has been collected (Section 7.4.6.13), combine it with the TCLP extract if they are compatible.

7.4.8.6 If the separate phase is not compatible with the TCLP extract, they must be stored and analyzed separately. The results of these analyses must be mathematically combined to determine final analyte concentrations. Apply the formula in Section 7.3.5.7.1 to obtain final results.

7.4.8.7 Discard the solid material remaining in the ZHE extractors.

7.4.8.8 Analyze the TCLP extract according to the appropriate analytical methods.

8.0 Quality Control/Quality Assurance/Corrective Action

8.1 Refer to the Laboratory Quality Management Plan (LQMP) for QC procedures and evaluations to be employed for this method.

8.1.1 Corrective Actions are those actions performed to correct situations that are deemed adverse to data quality. Corrective actions are addressed in section 10 of the LQMP and in the SOP "Non-conformance and Corrective Action." Corrective actions are usually addressed within the procedure section of the analytical SOP.

8.2 Blank Requirements

8.2.1 One blank is extracted prior to using an extractor vessel and then for every 20 TCLP extractions conducted on an extractor vessel. This applies to both volatile and nonvolatile extractor vessels.

8.2.2 One blank is extracted per SDG per extraction fluid. An additional blank is required for ZHE extractions.

8.2.3 A matrix spike must be analyzed with every 20 TCLP extractions or for each waste type (e.g. waste water, soil, etc.). Matrix spikes are added to the filtered, preserved TCLP extract after TCLP extraction and prior to application of method specific preparation procedures by the analyst performing those tasks.

9.0 Data Validation

9.1 Refer to the Quality Manual for data validation procedures and guidelines.

10.0 Training & Training Validation

10.1 Refer to the Laboratory Employee Training SOP for training procedures and guidelines.

11.0 Waste Management

11.1 Refer to the Waste Management Plan for waste disposal procedures.

12.0 Health and Safety

12.1 Refer to the Chemical Hygiene and Safety Plans for health and safety procedures and guidelines.

13.0 References

13.1 Solid Waste Manual, SW846 Update III, December 1996.

13.2 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements EM 200-1-3.

13.3 40 CFR Volume Part 261, Appendix II - Method 1311 Toxicity Characteristic Leaching Procedure.

Determination of pH

By SW-846 Method 9040C

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain.

2.0 Summary of Method

2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or combination electrode.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts of interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and solvents may be necessary.

3.2 Temperature effects on the electrometric measurement of pH arise from two sources.

3.3 The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and the temperature at the time of analysis.

4.0 Equipment and Apparatus

4.1 pH Meters, VWR Symphony/Orion 410A or equivalent

4.2 pH Probes, Orion 9165 BN or equivalent

4.3 Plastic cups

4.4 Thermometer Calibrated

5.0 Reagents and Standards

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination

5.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Procedure (SVQAP) This program is detailed in the Quality Manual.

5.3 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One of SW-846

5.4 Fisher pH Buffer Solutions at pHs of 4.00, 7.00 and 10.00.

5.5 Fisher pH Buffer Solutions at pH of 6.00 and 8.00.

5.6 Beakers

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

6.1.1 Refer to the Quality Manual for guidance concerning containers and preservation.

6.2 Holding Times

6.2.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.

7.0 Procedure

7.1 Calibrating pH Meters

7.1.1 Daily Calibration Procedures

Every day prior to sample analysis, the pH meter will be calibrated using a three point calibration. In order to complete this process, replace the buffers (# 4.00-pink, # 7.00-yellow, # 10.00-blue) with fresh buffer solution. Follow the manufacturer's instructions.

7.1.1.1 Set the meter to the appropriate buffer range following the manufacturer's instructions..

7.1.1.2 A slope reading will be given once the calibration is complete. Acceptance range is 94-103% R. If the slope is outside this range, recalibrate.

7.1.1.3 Once per week, do a verification check with a 6.00 and an 8.00 pH Buffers and record on the Daily Schedule. The acceptance criteria for all these buffers is +/- .05 pH units.

Note: Always store the probes in # 7.00 Buffer when not in use.

7.2 pH Analysis

7.2.1 Procedure

7.2.1.1 Record the client name/ID in the pH Logbook or worksheet

7.2.1.2 Obtain a clean cup and rinse the inside with a portion of the sample. Discard this rinsate.

7.2.1.3 Pour enough sample into cup to be able cover the sensing element of the electrode. Rinse the probe with deionized water and place the probe into the sample.

7.2.1.4 Press Measure; the meter will beep when done

7.2.1.5 Record the pH in the pH LogBook or worksheet

7.2.1.6 Rinse the probe with deionzed water and return the probe to the 7.00 Buffer.

7.2.1.7 Perform a duplicate analysis of the sample.

8.0 Quality Control/Quality Assurance

8.1 Refer to the laboratory's Quality Manual (QM) for QC procedures and evaluations to be employed for this method.

8.2 Corrective Actions are those actions performed to correct situations that are deemed adverse to data quality. Corrective actions are addressed in the QM and in the SOP "Non-conformance and Corrective Action." Corrective actions are usually addressed within the procedure section of the analytical SOP.

8.3 Perform a duplicate analysis of the pH buffers and the sample Repeat measurements on successive aliquots of sample until values differ by <0.1 pH units. Obtain an average and record on the worksheet.

9.0 Data Validation

9.1 Refer to the Quality Manual for data validation procedures and guidelines.

10.0 Training & Training Validation

10.1 Refer to the Employee Training SOP for training procedures and guidelines.

11.0 Waste Management

11.1 Refer to the Waste Management Plan for waste disposal procedures

12.0 Health and Safety

12.1 Refer to the Chemical Hygiene and Laboratory Safety Plans for health and safety procedures and guidelines.

13.0 References

13.1 Solid Waste Manual, SW846 Update III, December 1996.

13.2 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements Version 1.0 2 NOV 98

13.3 EPA, Methods for the Chemical Analysis of Water and Wastes, EPA 600-4-79-020.

14.0 Appendix

Soil and Waste pH by

SW-846 Method 9045D

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

Method 9045D is an electrometric procedure for the measurement of pH in soils and waste samples. Wastes may be classified as solids, sludges, or non-aqueous liquids. If water is present, it must not be greater than 20% of the total volume of the sample.

2.0 Summary of Method

The sample is mixed with reagent grade water and the resultant pH of the aqueous solution is measured.

3.0 Interferences and Potential Problems

3.1 Reagents, glassware and other sample processing hardware may yield artifacts of interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and may be necessary.

3.2 Samples with very low or high pH's may give false or incorrect readings on the meter

3.3 Temperature fluctuations may cause measurement errors.

3.4 Electrodes that become coated may cause erroneous readings. If an electrode becomes coated with an oily material that will not rinse free, the electrode can be cleaned (1) with an ultrasonic bath, or (2) be washed with detergent, rinses several times with water, placed in a 1.10 HCl so that lower third of the electrode in submerged, and then thoroughly rinsed with water, or (3) be cleaned per the manufacture' s instructions.

4.0 Equipment and Apparatus

4.1 VWR Symphony/Orion 410A or equivalent

4.2 Orion 9165 BN or equivalent

4.3 Beaker, 50-mL

4.4 Analytical balance: capable of weighing 0.1 g.

4.5 Variable speed stir-plate with Teflon coated stir bars

4.6 Glass fiber-filters and filtration system

4.7 Centrifuge

5.0 Reagents and Standards

5 1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One of SW-846.

5.2 Standard buffers at pH of 4.00, 7.00 and 10.00

6.0 Sample Preservation and Containers

6.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

6.1.1 Refer to the Quality Manual for guidance concerning containers, preservation and holding times.

6.2 Holding Times

6.2.1 Holding time for extraction is defined as the number of days from ***sample collection*** (e.g. sample date) to extraction.

6.2.2 Samples should be analyzed as soon as possible.

7.0 Procedure

7.1 Calibration – Follow the manufacturer's instructions for calibration.

Each instrument/electrode system must be calibrated at a minimum of three points that bracket the expected pH of the samples:

Calibration at pH of 4.00-7.00 and 10.00 buffers.

7.2 Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value. Sample temperature should be maintained at 25 +/- 1oC for an accurate reading.

8.0 Sample Preparation and pH measurement of soils

8.1 Precisely weight out 20.0 grams of a well-mixed soil sample in a clean beaker using a calibration analytical balance.

8.2 Add 20 mL of reagent water and continuously stir the suspension for 5 minutes If working with hygroscopic soils, salts or other problematic matrices, additional dilutions may be necessary.

8.3 Stop the stirring process and let the mixture stand for 1 hour to allow any suspensions to settle or filter or centrifuge off the aqueous phase for pH measurement.

8.4 Adjust the electrode on the clamp holder so that, upon the lower the electrode in to the beaker, the electrode will be immersed just deep enough in to the clear sample solution to establish a good electrical connection.

8.5 If the sample temperature differs by more than 2oC from the buffer solution, the measure pH must be corrected.

9.0 Sample preparation and pH measurement of waste materials

9.1 Measure out 20.0 grams of waste material in to a beaker and add 20 mL of reagent water.

9 2 Place a stir bar into the beaker and stir the suspension for 5 minutes. If working with hygroscopic soils, salts or other problematic matrices, additional dilutions may be necessary.

9.3 Let the waste mixture stand for 15 minutes to allow most of the suspended material to settle out from the suspension or filter/centrifuge off aqueous phase for pH measurement.

Note. If the waste is hygroscopic and absorbs all the reagent water, begin the analysis again using 20.0 g of waste and 40 mL of reagent water.

Note: If the supernant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned if it becomes coated with an oily material.

9.4 Adjust the electrode on the clamp holder so that, upon the lower the electrode in to the beaker, the electrode will be immersed just deep enough in to the clear sample solution to establish a good electrical connection .

9.5 If the sample temperature differs by more than 2oC from the buffer solution, the measure pH must be corrected.

10.0 Quality Control/Quality Assurance/Corrective Action

10.1 Refer to the laboratory's Quality Manual (QM) for QC procedures and evaluations to be employed for this method.

10.2 Corrective Actions are those actions performed to correct situations that are deemed adverse to data quality. Corrective actions are in the QM and in the SOP "Non-conformance and Corrective Action.".

10.3 Electrodes must be thoroughly rinsed between samples.

10.4 pH Meters must be calibrated using fresh buffers.

10.5 Perform duplicate analysis on the pH buffers and on the samples until the measurements are less than 0.1 pH units apart. Take the average and record on the worksheet.

11.0 Data Validation

11.1 Refer to the laboratory's QM for data validation procedures and guidelines.

12.0 Training & Training Validation

12.1 Refer to the Employee Training SOP and QM for training procedures and guidelines.

13.0 Waste Management

13.1 Refer to the Waste Management Plan for waste disposal procedures.

14.0 Health and Safety

14.1 Refer to the Chemical Hygiene and Laboratory Safety Plans for health and safety procedures and guidelines.

15.0 References

15.1 Solid Waste Manual, SW846 Update III, December 1996.

15.2 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements Version 1.0 2 NOV 98

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16.0 Appendix

Interim Guidance for the Determination of Reactive Sulfide from Wastes

SW 846 Method Chapter 7 Section 7.3.4 including Titration Method 9034

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

1.1 This method is applicable to all wastes, with the condition that such wastes, when combined with acids, do not explode or form explosive mixtures

1.2 This method provides a way to determine the specific rate of release of hydrogen sulfide upon contact with an aqueous acid.

1.3 This procedure releases only the hydrogen sulfide evolved at the test conditions. It is not intended to measure forms of sulfide other than those that are evolvable under the test conditions.

2.0 Summary of Method

2.1 An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. The analyte is quantified. The quantifying of sulfide is discussed in Section 10.0 of this Standard Operating Procedure.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts of interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and solvents may be necessary.

4.0 Equipment and Apparatus – Distillation Step

4.1 See Figure 1 in Appendix.

4.2 Round-bottom flask, 500-mL capacity, three neck, with 24/40 ground-glass joints.

4.3 Gas scrubber, 50-mL calibrated scrubber.

4.4 Stirring apparatus – To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motor driven propeller stirrer.

4.5 Addition funnel – with pressure-equalizing tube and 24/40 ground glass joint and Teflon sleeve.

4.6 Flexible tubing – For connecting the nitrogen supply with the apparatus

4.7 Water-pumped or oil-pumped nitrogen gas – with two-stage regulator.

4.8 Rotometer- for monitoring nitrogen gas flow rate.

4.9 Analytical balance – capable of weighing to 0.001 g

4.10 Graduated cylinder, 50-mL

5.0 Equipment and Apparatus – Titration Step

5.1 500-mL flasks

5.2 Hot plate stirrer

5.3 25 mL buret

5.4 Volumetric pipets

6.0 Reagents and Standards – Distillation Step

6.1 Reagent grade chemicals shall be used in all tests Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American

Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Procedure (SVQAP). This program is detailed in the Quality Manual.

6.3 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One of SW-846.

6.4 Sulfuric acid (0.01N), H2SO4: Add 2.8 mL concentrated H2SO4 to organic-free reagent water and dilute to 1 L. Withdraw 100 ml of this solution and dilute to 1 L to make the 0.01N H2SO4.

6.5 Sulfide Reference Solution: Dissolve 4.02 g of Na2S-9H2O in 1.0 L of organic-free reagent water. This solution contains 570-mg/L hydrogen sulfide. Dilute this stock solution to cover the analytical range required (100-570 mg/L).

6.6 Sodium Hydroxide Solution (1 25N), NaOH. Dissolve 50 g of NaOH in organic free water and dilute to 1 L with organic-free reagent water.

6.7 Sodium Hydroxide solution (0.25N), NaOH, Dilute 200 mL 1.25N sodium hydroxide solution to 1L with organic-free reagent water.

7.0 Reagents and Standards – Titration Step

7.1 Starch solution – Use either an aqueous solution or soluble starch powder mixture. Prepare an aqueous solution as follows: Dissolve 3 g of soluble starch and 2 g salicylic acid, as a preservative in 100 mL hot reagent water.

7.2 Iodine solution (0.025N)

7.3 Dissolve 25-g potassium iodide, KI, in 700 mL of reagent water in a 1-Liter volumetric flask. Add 3.2-g iodine. Allow to dissolve. Add 2 mL of 6N HCl acid. Dilute to 1L and standardize as follows

7.4 Dissolve approximately 2 g of KI in 150mL of reagent water. Add exactly 20 mL of the iodine solution (Section 7.2) to be titrated and dilute to 300 mL with reagent water.

7.4.1 Titrate with 0.025N standardized phenylarsine oxide or 0.025N sodium thiosulfate until the amber color fades to yellow. Add starch indicator solution. Continue titration drop by drop until the blue color disappears.

7.4.2 Run in replicate.

7.4.3 Calculate the normality as follows:

$$\text{Normality (I2)} = \frac{\text{mL of titrant x normality of titrant}}{\text{Sample size in mL}}$$

7.5 Sodium sulfide nonanhydrate – For the preparation of standard solutions to be used for calibration curves. Standards must be prepared at pH>9 and <11. Protect standard from exposure to oxygen by preparing it without headspace. These standards are unstable and should be prepared daily.

7.6 Titrant:

7.6.1 Standard phenylarsine oxide solution (PAO at 0 025N) is available commercially.

CAUTION: PAO is toxic.

7.6.2 Standard Sodium Thiosulfate Solution (0.025N). Dissolve 6 205 +/- .005g in 500-mL reagent water. Add 9 mL 1N NaOH and dilute to 1 liter.

8.0 Sample Preservation and Containers

8.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

8.1.1 Refer to section the Quality Manual for guidance concerning containers, preservation and holding times.

8.1.2 Samples containing, or suspected of containing, sulfide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, assuring no headspace exist and stoppered.

8.2 Holding Times

8.2.1 Analysis should start as soon as possible, and samples should be kept in a cool, dark place until analysis.

8.2.2 It is suggested that samples of sulfide wastes be tested as soon as possible. Although they can be preserved by adjusting the sample pH to 12 with a strong base and adding zinc acetate to the samples, these will cause the original sample to be diluted, increase the ionic strength, and possibly change other physical or chemical characteristics of the waste which may affect the rate of release of the hydrogen sulfide. Storage of samples should be under refrigeration and in the dark.

8.2.3 It is suggested that testing be conducted under a hood.

9.0 Procedure – Distillation Step

9 1 Add 50 mL of 0.25N NaOH solution to a calibrated scrubber and dilute with organic free reagent water to obtain an adequate depth of liquid.

9.2 Assemble the system and adjust the flow rate of nitrogen, using the rotometer. Flow rate should be at 60 mL/min.

9.3 Add 10 g of the waste to be tested to the system

9.4 With the nitrogen flowing, add enough sulfuric acid to fill the flask half full, while starting the 30-minute test period.

9.5 Begin stirring while the acid is entering the round-bottom flask. The stirring speed must remain constant throughout the test.

Note. The stirring should not be fast enough to create a vortex

9.6 After 30 minutes, close off the nitrogen and disconnect the scrubber Determine the amount of sulfide in the scrubber by the procedure described in the titration section.

10.0 Procedure – Titration Step

10.1 The following iodometric titration procedure is used to quantify the sulfide concentration in the distillate generated in the distillation procedure.

10.2 Pipet a known amount of standardized 0.025N iodine solution in a 500-mL flask, adding an amount in excess of that needed to oxidize the sulfide. Add enough reagent water to bring the volume to 100 mL. The volume of standardized iodine solution should be about 65 mL for samples with 50 mg of sulfide.

10 3 The trapping solution must be brought to a pH of 2 before proceeding. Titrate a small aliquot of the trapping solution to a pH 2 end point with 6N HCl and calculate the amount of HCl needed to acidify the

entire scrubber solution. Combine the small acidified aliquot with the remainder of the acidified scrubber solution.

10.4 Pipet the gas scrubbing solutions obtained to the flask, keeping the end of the pipet below the surface of the iodine solution. If at any point in transferring the zinc acetate solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Section 10.2 for calculations. Record the total volume of standardized 0.025N iodine solution used.

10.5 Prepare a rinse solution of a known amount of standardized 0.025N iodine solution, 1 mL of 6N HCl and reagent water to rinse the remaining white precipitate (zinc sulfide) from the gas scrubbing bottles into the flask. There should be no visible traces of precipitate after rinsing.

10.6 Rinse any remaining traces of iodine from the gas scrubbing bottles with reagent water, and transfer the rinsate to the flask.

10.7 Titrate the solution in the flask with standard 0.025N phenylarsine oxide or 0.025N sodium thiosulfate solution until the amber color fades to yellow. Add enough starch indicator for the solution to turn dark blue and titrate until the blue disappears. Record the volume of titrant used.

11.0 Quality Control-Quality Assurance

11.1 Refer to the laboratory's Quality Manual (QM) for QC procedures and evaluations to be employed for this method.

11.2 A summary of detection limits, spike concentrations and control limits are provided in Appendix A to this SOP.

11.3 Corrective Actions are those actions performed to correct situations that are deemed adverse to data quality. Corrective actions are addressed in section 10 of the LQMP and in the SOP "Non-conformance and Corrective Action." Corrective actions are usually addressed within the procedure section of the analytical SOP.

11.4 A reagent blank should be analyzed once in twenty analyses or per analytical batch, whichever is more frequent.

11.5 Check standards are prepared from water and a known amount of sodium sulfide. A check standard should be run with each analytical batch of samples, or once in twenty samples. Acceptable recovery will depend on the level and matrix.

11.6 A matrix spiked sample should be analyzed for each analytical batch or twenty samples, whichever is more frequent, to determine matrix effects. If recovery is low, acid-insoluble sulfides are indicated. A matrix spiked sample is a sample brought through the whole sample preparation and analytical process.

12.0 Calculations

12.1 Calculate the concentration of sulfide using the following equation:

$$\frac{(mL\ I2 \times N\ I2) - (mL\ titrant \times N\ titrant) \times \left[\frac{(32.06\ g)}{2\ eq.}\right]}{\text{sample weight (kg) or sample volume (L)}} = \text{sulfide (mg/Kg or mg/L)}$$

13.0 Data Validation

13.1 Refer to the laboratory's Quality Manual for data validation procedures and guidelines

14.0 Training & Training Validation

14.1 Refer to the Employee Training SOP for training procedures and guidelines.

15.0 Waste Management

15.1 Refer to the Waste Management Plan for waste disposal procedures.

16.0 Health and Safety

16.1 Refer to the Chemical Hygiene and Laboratory Safety Plans for health and safety procedures and guidelines.

17.0 References

17.1 Solid Waste Manual, SW846 Update III, December 1996, Method 7.3.4 and 9034.

17.2 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements Version 1.0 2 NOV 98

18.0 Appendix

Interim Guidance for the Determination of Reactive Cyanide

SW 846 Chapter 7.0 Section 7.3.3 and Method 9014

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

1.1 This method is applicable to all wastes, with the condition that wastes combined with an acid does not form an explosion or an explosive mixture.

1.2 This method provides a way to determine the specific rate of release of hydrocyanic acid upon contact with an aqueous acid.

1.3 This test measures only the hydrocyanic acid evolved at the test conditions. It is not intended to measure forms of cyanide other than those that are evolvable under the test conditions.

2.0 Summary of Method

2.1 An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. This generated gas contains hydrocyanic acid in the presence of water. This cyanide bearing acid is converted to cyanogen chloride by reaction of cyanide using Chloramine-T. After this reaction is completed color is formed with the addition of pyridine-barbituric acid. The analyte is then quantitated using the spectrophotometric procedure at 578 nm.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts of interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and solvents may be necessary.

4.0 Equipment and Apparatus – Distillation Apparatus

4.1 Round-bottom flask – 500 mL, three-neck, with 24/40 ground-glass joint Teflon sleeves.

4.2 Gas scrubber – 50 mL calibrated scrubber.

4.3 Stirring apparatus – To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motor-driven propeller stirrer.

4.4 Addition funnel – With pressure-equalizing tube and 24/40 ground-glass joint and Teflon sleeve.

4.5 Flexible tubing – For connection from nitrogen supply to distillation apparatus.

4.6 Water-pumped or oil-pumped nitrogen gas – with two-stage regulator.

4.7 Rotometer - For monitoring nitrogen gas flow rate.

4.8 Analytical balance – capable of weighing to 0.001 g

5.0 Equipment and Apparatus – Spectrophotometric Determination

5.1 Spectrophotometer – Spec 20, capable of measuring at 578 nm with a 1.0 cm cell.

5.2 Hotplate stirrer

5.3 pH meter

5.4 5-mL buret

5.5 Class A volumetric flasks at 100, 250 and 100-mL capacities

5.6 Erlenmeyer flask – 500 mL

6.0 Reagents and Standards – Distillation Procedure

6.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Procedure (SVQAP). This program is detailed in the Quality Manual.

6.3 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One of SW-846.

6 4 Sulfuric acid (0.01N): Add 2.8 mL concentrated sulfuric acid to organic-free reagent water.

6.5 Cyanide reference solution, (1000mg/L). Dissolve approximately 2.5 g of KOH and 2.51 g of KCN in 1 L of reagent water. Standardize with 0.0192N Silver Nitrate. Cyanide concentration equal to 1 mg/mL.

6.6 Sodium hydroxide solution (1.25N) NaOH. Dissolve 50 g of NaOH in reagent water and dilute to 1 L with reagent water.

6.7 Sodium Hydroxide Solution (0 25N) NaOH. Dilute 200 mL of 1.25N NaOH to 1L of reagent water.

6.8 Silver Nitrate Solution (0.0192N). Prepare by crushing approximately 5 g of Silver Nitrate crystals and drying to constant weight at 40oC. Weight 3.265 g of dried silver nitrate, dissolve in reagent water and dilute to 1 liter.

7.0 Reagents and Standards – Spectrophotometric Procedure

7.1 Sodium hydroxide solution (0 25N), NaOH. Dissolve 10g in 1 L of reagent water.

7.2 Sodium phosphate monobasic (1M) Dissolve 138 g of sodium phosphate monobasic in 1 L of reagent water.

7.3 Chloramine-T Solution (0.44%) Dissolve 1.0 g of white, water soluble Chloramine-T in 100 mL of water and refrigerate until ready to use

7 4 Pyridine-Barbituric acid reagent. Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix Add 15 mL of concentrated hydrochloric acid, mix, and cool to room temperature. Dilute to 250 mL with water. This reagent is stable for approximately six months if stored in a cool, dark place.

7.5 Stock potassium cyanide solution (1mL = 1000 ug CN), KCN. Dissolve 2.51 g of KCN and 2 g of KOH in 900 mL of water. Standardize with 0 0192N silver nitrate. Dilute to appropriate concentration to achieve 1 mL = 1000 ug of CN.

7.6 Intermediate standard potassium cyanide solution, (1 mL = 100 ug CN), KCN. Dilute 100 mL of stock potassium cyanide solution to 1000 mL with reagent water

7 7 Working standard potassium cyanide solution, (1 mL = 10 ug CN), KCN. Prepare fresh daily by diluting 100 mL of intermediate standard potassium cyanide solution and 10 mL of 1N NaOH to 1L with water.

8.0 Sample Preservation and Containers

8.1 As a rule, LMP, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

Samples containing or suspected of containing sulfide or a combination of sulfide and cyanide wastes

should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all headspace, and stoppered.

8.2 Holding Times

8.2.1 Analysis should commence as soon as possible.

8.2.2 Samples should be kept in a cool, dark place until analysis.

8.2.3 Although samples can be preserved with a strong base to a pH to 12, this will cause dilution of the sample, increase the ionic strength and possibly change other physical or chemical characteristics of the waste which may affect the rate of release of the hydrocyanic acid. Store in a refrigerator at 4oC.

8.2.4 Testing should be under a hood.

9.0 Procedure – Distillation

9.1 Add 50 ml of 0.25N NaOH solution to a calibrated scrubber and dilute with reagent water to obtain an adequate depth of liquid.

9.2 Close the system and adjust the flow rate of nitrogen, using the rotometer. Flow should be 60 mL/min.

9.3 Add 10 g of the waste to be tested to the system.

9.4 With the nitrogen flowing, add enough sulfuric acid to fill the flask half full. Start the 30-minute test period.

9.5 Begin stirring while the acid is entering the round-bottom flask. The stirring speed must remain constant throughout the test.

NOTE: The stirring should not be fast enough to create a vortex.

9.6 After 30minutes, close off the nitrogen and disconnect the scrubber. Determine the amount of cyanide in the scrubber by the spectrophotometric method detailed in Section 10.0.

10.0 Procedure – Spectrophotometric

10.1 Pipet a 50mL aliquot of the sample obtained from the distillation process into a 100-mL volumetric flask. If is the sample is later found to be beyond the linear range of the colormetric determination and redistillation of a smaller sample is not feasible, a smaller aliquot may be taken. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution.

NOTE: Temperature of reagents and spiking solutions can affect the response factor of the colormetric determination. The reagents stored in the refrigerator should be warmed to ambient temperature before use. Samples should not be left in a warm instrument to develop color, but instead they should be aliquoted to a cuvette immediately prior to reading the instrument.

10.2 Add 15 mL of 1M sodium phosphate solution and mix. Add 2 mL of Chloramine-T and mix. Some distillates may contain compounds that have chlorine demand. One minute after the addition of Chloramine-T, test for excess chlorine with KI-starch paper. If the test is negative, add 0.5 mL Chloramine-T. After one minute recheck with KI paper Continue to add Chloramine-T in 0.5-mL increments until excess is maintained. After 1 or 2 minutes, add 5 mL of pyridine-barbituric acid solution and mix

10.3 Dilute to 100 mL with reagent water and mix again Allow 8 minutes for color development and then read the absorbance at 578nm in a 1-cm cell within 15 minutes. The sodium hydroxide concentration will be 0.125N

11.0 Standard curve for samples without sulfide

11.1 Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

mL of Working Standard Solution (1 mL = 10 ug CN)	Concentration (ug CN/L)
0	Blank
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

11.2 After the standard solutions have been prepared according to the table above, pipet 50-mL of each standard solution into a 100-mL volumetric flask and proceed to Sections 10.2 and 10.3 to obtain absorbance values for the standard curve. The final concentrations for the standard curve will be one half of the amounts in the above table (final concentrations ranging from 20 – 400 ug/L).

11.3 Prepare a standard curve ranging from 20- 400 ug/L by plotting absorbance of standard versus the cyanide concentration.

12.0 Standard curve for samples with sulfide

12.1 It is important that all standards be distilled in the same manner as the samples using the method of standard additions. Standards distilled by this method will give a linear curve, at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

12.2 Prepare a series of standards similar in concentration to those mentioned in Section 11.1 and analyze and in Section 10.0. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration

12.3 Calculation – If the spectrophotometric procedure is used, calculate the cyanide, in ug/L, in the original sample as follows:

$$CN\ (ug/L) = \frac{A \times B}{E}$$

Where: A = ug/L CN read from standard curve
B = mL of sample after preparation of colorimetric analysis (100 mL recommended)
C = mL of sample after distillation (250 mL recommended)

13.0 Quality Control/Quality Assurance

13.1 Refer to the Laboratory's Quality Manual (QM) for QC procedures and evaluations to be employed for this method.

13.2 A summary of detection limits, spike concentrations and control limits are provided in Appendix A to this SOP

13 3 Analyze check standards with every analytical batch of samples If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

13.4 Analyze one duplicate sample for every 20 samples. The RPD of the replicates should be 20% or less. If this criterion is not met, the samples should be reanalyzed.

13.5 Analyze one matrix-spiked sample every 20 samples to check the efficiency of sample distillation procedure and to monitor potential matrix interference.

13.6 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interference such as samples which contain sulfides.

13.7 Corrective Actions are those actions performed to correct situations that are deemed adverse to data quality. Corrective actions are addressed in theQM and in the SOP "Non-conformance and Corrective Action." Corrective actions are usually addressed within the procedure section of the analytical SOP.

14.0 Data Validation

14.1 Refer to the Laboratory's Quality Manual for data validation procedures and guidelines.

15.0 Training & Training Validation

15.1 Refer to the Employee Training SOP for training procedures and guidelines.

16.0 Waste Management

16.1 Refer to the Waste Management Plan for waste disposal procedures.

17.0 Health and Safety

17.1 Refer to the Chemical Hygiene and Laboratory Safety Plans for health and safety procedures and guidelines.

18.0 References

18.1 Solid Waste Manual, SW846 Update III, December 1996 Chapter 7.0 Section 7.3.3

18.2 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements Version 1.0.2 NOV 98

19.0 Appendix

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Ignitability by SW-846

Method 1010

Prepared by: _____
Michael Kauffman, Technical Director

Approval: _____
Scott McKee, President

1.0 Scope and Application

The closed-cup tester is used to determine the flashpoint of solids or liquids, including those that tend to form a surface film under test conditions. Liquids containing solids are also tested using this method.

2.0 Summary of Method

A sample is heated at a slow, constant rate while stirring to keep homogeneous. A small flame is directed into the cup at regular intervals while interrupting the stirring. The flashpoint is the lowest temperature at which the vapor above the sample ignites.

3.0 Interferences and Potential Problems

3.1 Solvents, reagents, glassware and other sample processing hardware may yield artifacts of interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and solvents may be necessary.

3.1.1 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced

3.1.2 Glassware contamination can result in analyte degradation: Soap residue on glassware may cause degradation of certain analytes This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem. Chromic acid that is not completely rinsed will cause similar problems with analyte degradation and should be carefully rinsed to avoid this problem Refer to the SOP for cleaning of laboratory glassware: Sogcln03.doc

3.1.3 The unit must be cleaned well with methanol following the analysis of the p-Xylene standard to prevent leaving a flammable residue in the cup that might not be completely removed by just soap and water.

3.1.4 Any sample that flashes, particularly if it has a high solvent content, is a potential source of contamination Again, the analyst must take care to properly clean the entire apparatus, not just the cup itself.

3.1.5 Certain samples melt and adhere to the cup as they are heated. They must be removed in their entirety and the unit cleaned thoroughly or else contamination will result.

3.1.6 While most samples that ignite give a definite flash, there are others that leave some doubt. Since so many factors can create "false" flashes that are similar to the flashes of these ambiguous samples, if the analyst has any doubt at all, the supervisor should be consulted.

4.0 Equipment and Apparatus

4.1 Equipment

4.1.1 Pensky-Martens Closed Cup Apparatus

5.0 Reagents and Standards

5.1 Policy.

5.1.1 Reagent grade chemicals shall be used in all tests Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents

of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents/solvents/standards must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

5.1.2 All reagents/solvents/standards must be traceable using the Solution Validation Quality Assurance Program (SVQAP). This program is detailed in the Quality Assurance Program Plan Section 6.3. Refer to SOP Qasrpt02.doc, "*Standard and Reagent Preparation and Traceability*".

5.2 Reagents

5.3 P-Xylene, Reagent grade.

5.4 Methanol, Reagent grade.

6.0 Sample Preservation and Containers

6.1 As a rule, Environmental Testing and Consulting, Inc. does not engage in sampling activities. However, each analytical method has specific container and preservation (chemical and/or temperature) requirements.

6.1.1 Refer to Chapter 2 of SW-846 for guidance concerning containers, preservation and holding times. A PDF version of this Chapter is available: Server\ETC_SOP\SW-846\Chap2.PDF. Refer to Table 2-36 (pages 48 & 49).

6.2 Holding Times

6.2.1 Holding Time for extraction is defined as the number of days from ***Sample Collection*** (e g Sample Date) to extraction.

6.2.2 Holding Time for analysis of this parameter is 7 days. Collect samples in glass No preservative is needed.

7.0 Procedure

7.1 The closed-cup must be rinsed with methanol and then cleaned with soap and water before use. The top of the apparatus, including the metal stirrer, should also be rinsed with methanol and DI to remove any potential contamination from prior samples.

7.2 Place the sample in the closed-cup, which should be at room temperature and heat slowly while stirring occasionally.

7.3 The flame should be directed into the cup at one-degree intervals to determine if the sample ignites. A true flash is usually (but not always) very obvious. The analyst should be careful not to report false flashes, such as those caused by the flame blowing out, the reignition of the flame by the pilot light after it's blown out, etc. If there is any doubt about whether a sample actually ignited, a supervisor should be consulted.

7.4 If the sample ignites, the above procedure is repeated as all positive results must be run in duplicate. The second result is recorded and the supervisor must initial the worksheet in the space provided.

8.0 Quality Control

8.1 p-Xylene is used as a standard for flashpoint (flashpoint of p-Xylene = 27oC) and recorded on the work sheet.

8.2 The acceptable range for the p-Xylene standard is +/- 1 degree. Unacceptable results should be

reanalyzed immediately, and any further problems should be promptly reported to the supervisor. In the event that a sample ignites at >90oC (very near the regulatory level) the acceptable range for the p-Xylene standard shall be revised to +/- 0.5 degrees

8.3 Duplicate analyses are performed on all positive samples.

9.0 Calculations

Not applicable Temperature of ignition is read off thermometer

10.0 Data Validation

Refer to Laboratory's Quality Manual.

11.0 Waste Management

Refer to the Waste Management Plan.

12.0 Health and Safety

Consult the Chemical Hygiene Plan and Laboratory Safety Plans.

13.0 Training & Training Validation

Refer to the Employee Training SOP.

14.0 References

14.1 *"Carcinogens – Working with Carcinogens"*, Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No 77-206, August 1977.

14.2 "OSHA Safety and Health Standards, General Industry", 29 CFR 1910.

14.3 *"Proposed OSHA Safety and Health Standards, Laboratories"*, Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986

14.4 *"Safety in Academic Chemistry Laboratories"*, American Chemical Society Publication, Committee on Chemical Safety.

14.5 Solid Waste Manual, SW846 Update III, December 1996.

14.6 Code of Federal Regulations 40 CFR Part 136.

14.7 U.S. Army Corps of Engineers (USACE) Shell for Chemical Analytical Requirements, Appendix H.

15.0 Appendix

APPENDIX D

TABLES I-1 THROUGH I-7 OF THE USACE SHELL ANALYTICAL REQUIREMENTS

Table I-1
Summary of Measurement quality objectives for Method 6010 Inductively Coupled Plasma (ICP) Metals

Quality Control Element	Description of Element	Frequency of Implementation	Acceptance Criteria
Initial Calibration (I.9.2.1.1)	Option 1- 1 std and blank, and a low-level check standard at MQL Option 2- 3 stds and blank	Daily	Option 1- Low-level check standard ± 20% Option 2- r • 0.995
Instrumental Precision (I 9.2.1.1)	%RSD 3 integrations (exposures)	Each calibration and calibration verification standards (ICV/CCV)	%RSD < 5%
Initial Calibration Verification (ICV) (I.9.3)	Midlevel (2nd source) verification	After initial calibration	%Recovery ± 10%
Initial Calibration Blank (ICB) (I 9.4)	Interference-free matrix to assess analysis contamination	After initial calibration	Analytes < MDL
Interelement Check Standards (ICS) (I 8.1)	ICS-A - interferents only ICS-B - interferents and target analytes	Beginning of analytical sequence	%Recovery ± 20% for target analytes
Continuing Calibration Blank (CCB) (I.9.4)	Interference-free matrix to assess analysis contamination	Every 10 samples and at end of analytical sequence	Analytes < MDL
Continuing Calibration Verification (CCV) (I.9.5 / I 9.5.1)	Midlevel verification	Every 10 samples and at end of analytical sequence	%Recovery ± 10%
Method Blank (MB) (I 10 2 1 / I 11.4 1)	Interference-free matrix to assess overall method contamination	1 per sample batch	Analytes < one-half MRL
Laboratory Control Sample (LCS) (I.10.2 2 / I 11 4.2)	Interference-free matrix containing all target analytes	1 per sample batch	%Rec = 80% - 120% Sporadic marginal failures[1] %Rec = 60% - 140%
Matrix Spike (MS) (I 10.2.3 / I 11 4 3 / I.11.4.3.1)	Sample matrix spiked with all/subset of target analytes prior to digestion	1 per sample batch	%Rec = 75% - 125%
Matrix Duplicate (MD) or Matrix Spike Duplicate (MSD) (I 10 2.4 / I.11 4 4)	Refer to text for MD or MS	1 per sample batch	RPD • 25%
Post Digestion Spike (PDS) (I.10.3.1 / I.11 4 6)	Sample digestate spiked with all/subset of target analytes	1 per sample batch on MS sample	%Rec = 75% - 125%
Serial Dilution (SD) (I.10.3 2)	1:4 dilution analyzed to assess matrix effects	As needed to assess new and unusual matrices	Agreement between undiluted and diluted results ± 10%
Method of Standard Additions (MSA) (I.12.2 1)	Method of quantitation	As needed for samples with suspected or confirmed matrix effects	r • 0 995

[1] The number of Sporadic Marginal Failure (SMF) allowances depends upon the number of target analytes reported from the analysis. For instance, if between 7 to 15 metals are reported from the ICP analysis, one (1) SMF is allowed to the expanded criteria presented. If greater than 15 metals are reported from the ICP analysis, two (2) SMFs are allowed.

Table I-2
Summary of Measurement quality objectives for Method 7010/7470/7471 Series GFAA/CVAA Metals

Quality Control Element	Description of Element	Frequency of Implementation	Acceptance Criteria
Initial Calibration (I.9.2 1.2)	3 stds and blank(GFAA) 5 stds and blank(CVAA)	Daily	r • 0 995
Instrumental Precision (I.9.2.1 2)	RPD of 2 injections	All standards, and ICV/CCV	RPD ± 10%
Initial Calibration Verification (ICV) (I 9 3)	Midlevel (2nd source) verification	After initial calibration	%Rec ± 10%
Initial Calibration Blank (ICB) (I 9 4)	Interference-free matrix to assess analysis contamination	After initial calibration	Analytes < MDL
Continuing Calibration Blank (CCB) (I 9.4)	Interference-free matrix to assess analysis contamination	Every 10 samples and at end of analytical sequence	Analytes < MDL
Continuing Calibration Verification (CCV) (I 9 5 / I.9 5.1)	Midlevel verification	Every 10 samples and at end of analytical sequence	%Rec ± 20%
Method Blank (MB) (I 10.2 1 / I 11 4 1)	Interference-free matrix to assess overall method contamination	1 per sample batch	Analytes < one-half MRL
Laboratory Control Sample (LCS) (I.10.2.2 / I.11 4.2)	Interference-free matrix containing target analytes	1 per sample batch	%Rec = 80% - 120%
Matrix Spike (MS) (I 10.2 3 / I 11 4 3 / I 11 4 3 1)	Sample matrix spiked with target analytes prior to digestion	1 per sample batch	%Rec = 80% - 120%
Matrix Duplicate (MD) or Matrix Spike Duplicate (MSD) (I 10 2 4 / I 11 4 4)	Refer to text for MD or MS	1 per sample batch	RPD • 20%
Post Digestion Spike (PDS) (I.10.3.1 / I 11 4 6)	Sample digestate spiked with target analytes	Every sample	%Rec = 85% - 115%
Serial Dilution (SD) (I.10 3.2)	1.4 dilution analyzed to assess matrix effects	As needed to assess new and unusual matrices	Agreement between undiluted and diluted results ± 10%
Method of Standard Additions (MSA) (I 12 2.1)	Method of quantitation	As needed for samples with suspected or confirmed matrix effects	r • 0 995

Note: GFAA = Graphite furnace - atomic absorption spectroscopy
CVAA = Cold vapor - atomic absorption

Table I-3
Summary of Measurement quality objectives for Method 8021 VOCs

QC Element	Target Analyte/Surrogate	Poor Purgers/Gases/Sporadic Marginal Failures[1]
Initial Calibration (I.9.2.2.1)	Primary Evaluation: r • 0.995, %RSD • 20%, r^2 • 0.990	No allowance
	Alternative Evaluation: Mean %RSD for all target analytes • 20%	Alternative Evaluation: Maximum allowable %RSD for each target analyte • 40%
ICV (I.9.3)	%Rec = 85% - 115%	No allowance
CCV (I.9.5 / I.9.5.2 / I.9.5.2.1)	Primary Evaluation: %Drift • 15%, %D • 15%	Primary Evaluation: %Drift • 20%, %D • 20%
	Alternative Evaluation: Mean %Drift/%D for all target analytes • 15%, with maximum allowable restriction noted at right for individual analytes.	Alternative Evaluation: Maximum allowable %Drift/%D for each individual target analytes • 30%
MB (I.10.2.1 / I.11.4.1)	Target Analytes: Analytes < one-half MRL	Common Lab Contaminants: Analytes < MRL
LCS (I.10.2.2 / I.11.4.2)	Water: %Rec = 80% - 120% Solids: %Rec = 75% - 125%	Sporadic Marginal Failures[1]: %Rec = 60% - 140%
MS (I.10.2.3 / I.11.4.3 / I.11.4.3.2)	%Rec = 70% - 130%	Sporadic Marginal Failures[1]: %Rec = 60% - 140%
MSD/MD (I.10.2.4 / I.11.4.4)	Water: RPD • 30% Solids: No RPD Limits	Water: RPD • 40% Solids: No RPD Limits
Surrogates (I.10.2.5 / I.11.4.5)	Interference-Free Matrix: Water: %Rec = 80% - 120% Solids: %Rec = 75% - 125% Project Sample Matrix %Rec = 70% - 130%	Not applicable
Target Analyte Confirmation (I.12.3)	RPD • 40%	RPD • 40%

[1] The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported from the analysis. For instance, if the 8020 Target Analyte List (10 compounds) is reported, 1 SMF is allowed. If the 8010 Target Analyte List (32 compounds) is reported, 3 SMFs are allowed. If the full 8021 Target Analyte List (60 compounds) is reported, 4 SMFs are allowed. If the MS includes only a subset of compounds, allow only 1 SMF for that QC element..

Table I-4
Summary of Measurement quality objectives for Method 8081 Pesticides

QC Element	Target Analyte/Surrogate	Sporadic Marginal Failure [1]
DDT/Endrin %Breakdown (I.8.2)	DDT & Endrin %Breakdown • 15% each	Not Applicable
Initial Calibration (I.9 2.2 4)	Primary Evaluation r • 0 995, %RSD • 20%, r^2 • 0.990	No allowance
	Alternative Evaluation: Mean %RSD for all target analytes • 20%, with maximum allowable restriction noted at right for individual analytes	Alternative Evaluation: Maximum allowable %RSD for each individual target analyte • 40%
ICV (I.9 3 / I 9.3 1)	%Rec = 85% - 115%	No allowance
CCV (I 9 5 / I.9.5.2 / I 9 5.2.2)	Primary Evaluation: %Drift • 15%, %D • 15%	No allowance
	Alternative Evaluation: Mean %Drift/%D for all target analytes • 15%, with maximum allowable restriction noted at right for individual analytes	Alternative Evaluation: Maximum allowable %Drift/%D for each individual target analyte • 30%
MB (I 10 2.1 / I 11.4.1)	Analytes < one-half MRL	Not applicable
LCS (I 10 2.2 / I 11 4 2)	Water: %Rec = 50% - 130% Solids: %Rec = 50% - 130%	Sporadic Marginal Failures[1] %Rec = 30% - 150%
MS (I 10 2.3 / I 11 4.3 / I 11.4 3 2)	%Rec = 40% - 140%	Sporadic Marginal Failures[1] %Rec = 30% - 150%
MSD/MD (I 10.2 4 / I 11 4 4)	RPD • 50%	RPD • 60%
Surrogates (I 10 2 5 / I 11.4 5)	Interference-Free Matrix Water: %Rec = 50% - 130% Solids %Rec = 50% - 130% Project Sample Matrix: %Rec = 40% - 140%	Not applicable
Target Analyte Confirmation .(I.12 3)	RPD • 40%	RPD • 40%

[1] The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported from the analysis. For instance, if the full list of 21 compounds is reported from the GC/electron capture detector analysis, then 2 SMFs are allowed to the expanded criteria presented. If the MS includes only a subset of compounds, allow only 1 SMF for that QC element.

Table I-5
Summary of Measurement quality objectives for Method 8082
PCBs

QC Element	Target Analyte/Surrogate
Initial Calibration (I 9 2.2 5)	r • 0.995, RSD • 20%, r^2 • 0.990
ICV (I.9.3 / I.9.3.2)	%Rec = 85% - 115%
CCV (I.9.5 / I 9 5 2)	%Drift • 15%, %D • 15%
MB (I.10.2.1 / I.11.4 1)	Analytes < one-half MRL
LCS (I.10.2.2 / I.11.4.2)	Water: %Rec = 50% - 130% Solids: %Rec = 50% - 130%
MS (I.10.2.3 / I.11.4.3)	%Rec = 40% - 140%
MSD/MD (I.10.2.4 / I 11 4 4)	RPD = 50%
Surrogates (I.10 2.5 / I.11.4.5)	Interference-Free Matrix: Water: %Rec = 50% - 130% Solids: %Rec = 50% - 130% Project Sample Matrix: %Rec = 40% - 140%
Target Analyte Confirmation (I.12.3)	RPD • 40%

Table I-6
Summary of Measurement quality objectives for Method 8260 VOCs

QC Element	Target Analyte/Surrogate	Poor Purgers/Gases/Sporadic Marginal Failures[1]
Initial Calibration (I.9 2 2.4)	Instrument Evaluation: System performance check compounds (SPCCs): minimum response factor (RF) values per method requirements Calibration check compounds (CCCs): verify %RSD • 30%	No allowance
	Primary Evaluation: r • 0 995, %RSD • 15%, r^2 • 0.990	No allowance
	Alternative Evaluation: Mean %RSD for all target analytes • 15%, with maximum allowable restriction noted at right for individual analytes.	Alternative Evaluation: Maximum allowable %RSD for each individual target analyte • 30%
ICV (I.9.3)	%Rec = 80% - 120%	No allowance
CCV (I 9 5 / I 9 5.2 / I 9 5 2 4)	Instrument Evaluation: SPCCs: minimum RF values per method requirements	No allowance
	Primary Evaluation (CCCs): %Drift • 20%, %D • 20%	No allowance
MB (I 10 2 1 / I 11 4.1)	Target Analytes: Analytes < one-half MRL	Common Lab Contaminants. Analytes < MRL
LCS (I 10.2 2 / I 11 4 2)	Water %Rec = 80% - 120% Solids: %Rec = 75% - 125%	Sporadic Marginal Failures[1] %Rec = 60% - 140%
MS (I 10 2 3 / I.11 4 3 / I 11.4 3 2)	%Rec = 70% - 130%	Sporadic Marginal Failures[1] %Rec = 60% - 140%
MSD/MD (I 10 2 4 / I 11 4 4)	Water: RPD • 30% Solids No RPD Limits	Water RPD • 40% Solids: No RPD Limits
Surrogates (I.10 2.5 / I 11 4 5)	%Interference-Free Matrix: Water: %Rec = 80% - 120% Solids: %Rec = 75% - 125% Project Sample Matrix: %Rec = 70% - 130%	Not applicable

[1] The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported from the analysis. For instance, if the full list of 68 compounds is reported from the GC/MS analysis, then 5 SMFs are allowed to the expanded criteria presented for the LCS. If the MS includes only a subset of compounds, allow only 1 SMF for this QC element

Table I-7
Summary of Measurement quality objectives for Method 8270 Semivolatiles

QC Element	Target Analyte/Surrogate	Poor Performers/Sporadic Marginal Failures[1]
Initial Calibration (I.9.2.2.7)	Instrument Evaluation: SPCCs: minimum RF values per method requirements CCCs: verify %RSD • 30%	No allowance
	Primary Evaluation (all target analytes) r • 0 995, %RSD • 15%, r^2 • 0.990	No allowance
	Alternative Evaluation Mean %RSD for all target analytes • 15%, with maximum allowable restriction noted at right for individual analytes	Alternative Evaluation: Maximum allowable %RSD for each individual target analyte • 40%
ICV (I.9.3)	%Rec = 70% - 130%	No allowance
CCV (I.9.5 / I.9.5.2 / I.9 5 2 4)	Instrument Evaluation SPCCs: minimum RF values per method requirements	No allowance
	Primary Evaluation (CCCs). %Drift • 20%, %D • 20%	No allowance
MB (I.10.2.1 / I.11 4 1)	Target Analytes. Analytes < one-half MRL	Common Lab Contaminants. Analytes < MRL
LCS (I 10 2.2 / I 11 4 2)	Water %Rec = 60% - 120% (~15 analytes) = 45% - 135% (~30 analytes) = 20% - 150% (~15 analytes) Solids %Rec = 60% - 120% (~20 analytes) = 45% - 135% (~25 analytes) = 30% - 150% (~15 analytes)	Sporadic Marginal Failures[1] Water: %Rec = 15% - 150% Solids: %Rec = 25% - 150%
MS (I 10 2.3 / I 11.4 3 / I 11 4 3 2)	Water %Rec = 45% - 135% Solids %Rec = 45% - 135%	Sporadic Marginal Failures[1] Water. %Rec = 15% - 150% Solids %Rec = 20% - 150%
MSD/MD (I.10.2.4 / I.11 4.4)	Water. RPD • 50% Solids. RPD • 60%	Sporadic Marginal Failures[1]: Water: RPD • 60% Solids. RPD • 60%
Surrogates (I.10.2.5 / I.11.4.5)	%Interference-Free Matrix[2]: Water: %Rec = 60% - 120% B/N cmpds %Rec = 45% - 135% A cmpds Solids: %Rec = 60% - 120% B/N cmpds %Rec = 45% - 135% A cmpds Project Sample Matrix[2] Water %Rec = 45% - 135% B/N cmpds %Rec = 35% - 140% A cmpds Solids %Rec = 45% - 135% B/N cmpds %Rec = 35% - 140% A cmpds	Sporadic Marginal Failures[1] Water: %Rec = 15% - 150% Solids. %Rec = 20% - 150%

[1] The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported from the analysis For instance, if the full list of target compounds as presented in Table 13 are reported, then 5 SMFs are allowed to the expanded criteria presented for the LCS If the MS includes only a subset of compounds and for Surrogates, allow up to 1 SMF
[2] B = base, N = neutral, and A = acid compounds (cmpds).

APPENDIX E

DATA QUALITY EVALUATION SOPs

DQE SW-846 Method 8260B Rev. 05/14/04
(Volatile Organic Compounds)

Initial Review by:_____Date:_____ SDG#_____
Senior Review by:_____Date:_____ Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
SW-846 8260B
(Volatile Organic Compounds)

Note: The following Data Quality Evaluation (DQE) for SW-846 8260B (VOCs) as performed by Severn Trent Laboratory – North Canton will be evaluated according to the COE Shell Document. Be aware that Method 8260B strictly limits GC/MS analytical time to a 12 hour window following a successful tune. Table 12 of the COE Shell Document is the summary of Method 8260B quality objectives. In lieu of copying materials from the SDG that are outside of the following QA/QC criteria, record the sequential page number/s provided on the bottom right hand corner of the SDG in the space provided to the right of the question.

1.0 Sample Integrity

					Notes
1.1	Yes ___	No ___	N/A ___	Was the method specific 14 day holding time met for VOCs in water? Were soil/sediment samples shipped to laboratory within 24 hrs of collection and analyzed or preserved within 48 hrs of receipt? If soil sample is preserved, holding time is 14 days after preservation. Holding time is calculated as time elapsed from sampling to analysis. If not, flag results J. Note: Holding time for unpreserved water samples is 7 days.	
1.1.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of VOC samples? [Water = 3 x 40 ml VOA vials with teflon lined caps, preserved with **HCl** to pH < 2 @ 4° C] [Soil = 4 x 5g EnCores™ (low-level) or 2 x 25g EnCores™ (high-level), preserved @ 4° C] Note: For soil or sediment, a separate 4 oz. jar (without headspace) must be collected to determine moisture content. Note: Preservation of soil/sediment samples after laboratory receipt may consist of 5 grams soil in DI water or sodium bisulfate (low level) or methanol (for high level analysis) or both.	
1.1.2	Yes ___	No ___	N/A ___	Was the pH checked in the laboratory after analysis (water only) and were all samples within the pH requirement? Note any outliers.	
1.1.3	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to VOC data results and proceed to next method in SDG.**	

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2.0 Laboratory Method

					Notes
2.1	Yes	No	N/A	Was the correct method used for analysis of VOCs? [SW-846: Water Prep Method 5030B/Analysis Method 8260B] [SW-846: Soil Prep Method 5035A/Analysis Method 8260B]	
2.2	Yes	No	N/A	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL. Results reported between the MDL and PQL are flagged J	

3.0 GC/MS Instrument Performance Check (Tune)

3.1	Yes	No	N/A	Did the laboratory include the GC/MS tuning and mass calibration form performed with 4-bromofluorobenzene (4-BFB) for the initial calibration and each daily 12 hour sequence? Note SDG page numbers.	
3.2	Yes	No	N/A	Did the tune pass the criteria as established in Method 8260B? Verify that the tuning criteria listed on the lab's form matches that of the method as follows:	

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

If tune criteria failed, reject (r) all associated data.

4.0 Initial Calibration

4.1	Yes	No	N/A	Are the Initial Calibration forms present with at least 5 calibration levels for volatiles? Record SDG page numbers.	
4.2	Yes	No	N/A	If a quadratic curve was used for any compound, have at least 6 standards been analyzed and included in the calibration of that compound?	

					Notes
4.3	Yes	No	N/A	Do the System Performance Check Compounds (SPCCs) meet the minimum Response Factor (RF) values per method requirements? The minimum mean Relative Response Factors (RRF) for the volatile SPCCs are 0.10 for chloromethane, 1,1-dichloroethane, and bromoform and 0.30 for chlorobenzene and 1,1,2,2-tetrachloroethane.	
4.4	Yes	No	N/A	Is the RSD for each individual Calibration Check Compound (CCC) less than or equal to 30%? The CCCs are vinyl chloride, 1,1-dichlorethene, chloroform, 1,2-dichloropropane, toluene, and ethylbenzene.	
4.5	Yes	No	N/A	If Average Response Factor (RF) for all other target analytes was used, is the RSD ≤ 15% **or** if a linear regression was used, is the initial calibration correlation coefficient (r) ≥ 0.995 (r^2 ≥ 0.990)? **Alternately**, the mean %RSD for all target analytes must be ≤ 15%, with no target analyte exceeding 30%RSD. If not, flag "J" all associated sample results for the specific compound failure and flag "R" associated samples results for failures >30%.	
4.6	Yes	No	N/A	Was an alternate source Initial Calibration Verification (ICV) check standard analyzed at the completion of a valid Initial Calibration? This standard is typically prepared at a concentration in the middle of the calibration range. Record SDG page numbers.	
4.7	Yes	No	N/A	Was the alternate source ICV within ± 20% of the true value? If not, flag results J. There are no allowances for SMF in the COE shell.	

5.0 Continuing Calibration

5.1	Yes	No	N/A	Was a Continuing Calibration Verification (CCV) analyzed at the beginning of each 12 hour sequence, before the analysis of samples?	
5.2	Yes	No	N/A	Are the Continuing Calibration Verification (CCV) forms present? Record SDG page numbers.	

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Notes

5.3	Yes	No	N/A	Do the System Performance Check Compounds (SPCCs) meet the minimum Response Factor (RF) values in the CCV per method requirements? The minimum response factors for the volatile SPCCs are 0.10 for chloromethane, 1,1-dichloroethane, and bromoform and 0.30 for chlorobenzene and 1,1,2,2-tetrachloroethane.	
5.4	Yes	No	N/A	Is the %D for each individual Calibration Check Compound (CCC) less than or equal to 20%? The CCCs are vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, and ethylbenzene.	
5.5	Yes	No	N/A	Are the remaining target analytes within 20%D if average RF is used or ± 20% drift if a linear or quadratic calibration is used? If it is and is less than 40% D or drift, then flag that compound in the 12 hour sequence as estimated (J). Any compound greater than 40%D or drift should be rejected (R) in that 12 hour sequence.	

6.0 Method Blanks

6.1	Yes	No	N/A	Is the Method Blank summary present? Record SDG page number	
6.2	Yes	No	N/A	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix in each 12 hour analytical sequence?	
6.3	Yes	No	N/A	Are the common laboratory contaminants (acetone, methylene chloride, 2-butanone, and sometimes freon) less than PQLs in the method blank? If greater than PQL, corrective action should have been taken (reanalysis of blank). List compounds present with concentration and associated samples and apply the following rule. If sample concentration is ≤ 10x the blank value, assign a "B". If sample concentration is > 10x the blank value, no flag is necessary	
6.4	Yes	No	N/A	Are target analytes less than PQLs in the method blank? If greater than PQL, corrective action should have been taken (reanalysis of blank). List compounds present with concentration and associated samples and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	

7.0 Laboratory Control Standard (LCS)

					Notes
7.1	Yes ___	No ___	N/A ___	Was the LCS and/or LCS duplicate summary form present? Record SDG page numbers.	
7.2	Yes ___	No ___	N/A ___	Was an LCS analyzed with each SDG or every 20 samples of similar matrix within each 12 hour sequence?	
7.3	Yes ___	No ___	N/A ___	For waters, are spiked recoveries within 80-120% in the LCS/LCSD? For soils, are spiked recoveries within 75-125% in the LCS/LCSD? If a full list of 68 compounds is being analyzed, then 5 failures are allowed within the Sporadic Marginal Failure limits (± 40%), as prescribed in the COE Shell document, Table 12. See section 9.3 of the COE Shell document for guidance if less than 68 compounds are present. Flag results only if **both** the LCS and LCSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the LCS = J Hits and NDs that fail low in the LCS = J	

8 0 Matrix Spikes

8.1	Yes ___	No ___	N/A ___	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Record SDG page numbers.	
8.2	Yes ___	No ___	N/A ___	Were MS/MSDs analyzed at a frequency of 1 per 20 samples as designated by project team? List samples that were spiked.	
8.3	Yes ___	No ___	N/A ___	Were the recoveries of the MS/MSD within COE limits of 70-130% for water or soil? If a full list of 68 compounds is being analyzed, then 5 failures are allowed within the Sporadic Marginal Failure limits (± 40% recovery), as prescribed in the COE Shell document. See section 9.3 for guidance if less than 68 compounds are present. Reference SDG page number. If recoveries are high, flag positive results in the parent sample "J". If recoveries are low, flag positive and non-detect results in the parent sample "J". NOTE: Control limits apply only when spike sample results fall within the normal calibration range. If dilutions are required due to high sample concentrations, the data are evaluated but no flags are applied.	

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					Notes
8.4	Yes	No	N/A	Was the RPD between the MS/MSD < 30% for water? The COE does not prescribe RPD limits for soil, however, RPD should generally not exceed 40%. If a full list of 68 compounds is being analyzed, then 5 failures are allowed within the Sporadic Marginal Failure limits (RPD less than or equal to 40%), as prescribed in the COE Shell document, Table 12. See section 9.3 of the COE Shell document for guidance if less than 68 compounds are present. If not, flag results J.	

9.0 Duplicates

9.1	Yes	No	N/A	Were any intra-laboratory or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC. Record and cross-reference sample ID along with SDG page numbers.	
9.2	Yes	No	N/A	Is RPD between sample and duplicate < 30%? If not, list sample ID, concentration of both samples and RPD. Record SDG page number/s. If RPD is greater than 30%, flag as estimated (J).	

10.0 Internal Standards and Surrogates

10.1	Yes	No	N/A	Are the internal standard summary forms present? Record SDG page numbers.	
10.2	Yes	No	N/A	Were the internal standard area counts from each standard, sample and blank within 2 times (–50% to +100%) that found in the mid-point standard of the most recent initial calibration? If not, flag associated compound results J of the affected IS.	
10.3	Yes	No	N/A	Were the internal standard retention times from each standard, sample and blank within 30 seconds of the retention time found in the mid-point standard of the most recent initial calibration? If not, flag associated compound results J of the affected IS.	
10.4	Yes	No	N/A	Are the Surrogate standard summary forms present? Record SDG page numbers.	

Notes

10.5 Yes ___ No ___ N/A ___ Were the Surrogate Standards from each standard, sample and blank within 80-120% recovery in "interference free" water matrices or 75-125% in "interference free" solid matrices? These matrices are considered the lab QC samples such as the method blanks, LCSs, CCVs, etc. and field QC samples such as trip blanks and rinsate blanks. No allowance for Sporadic Marginal Failures listed in the COE Shell Document Corrective action by the laboratory should be reanalysis of the sample.

10.6 Yes ___ No ___ N/A ___ Were the Surrogate Standards in "project sample matrix" within 70-130% recovery? No allowance for Sporadic Marginal Failures listed in the COE Shell Document. Corrective action by the laboratory should be reanalysis of the sample. If not, flag positive results J for recoveries above 130% and flag positive and non-detect results J for recoveries below 70%.

11.0 Compound Quantitation and Reported Detection Limits

11.1 Yes ___ No ___ N/A ___ Are results present for all samples sent to the lab for volatiles?

11.2 Yes ___ No ___ N/A ___ Have PQLs been adjusted to properly reflect sample dilutions?

11.3 Yes ___ No ___ N/A ___ Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis.

12.0 Field QA/QC

12.1 Yes ___ No ___ N/A ___ Were any rinsate blanks collected?

12.2 Yes ___ No ___ N/A ___ Are the common laboratory contaminants (acetone, methylene chloride, 2-butanone, and sometimes freon) present in the rinsate blank? List compounds present with concentration and affected samples and apply the following rule.
If sample concentration is $\leq$ 10x the blank value, assign a "B".
If sample concentration is > 10x the blank value, no flag is necessary

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					Notes
12.3	Yes	No	N/A	Are target analytes present in the rinsate blank? List compounds present with concentration and affected samples and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary.	
12.4	Yes	No	N/A	Were trip blanks shipped in the cooler with the field samples?	
12.5	Yes	No	N/A	Are the common laboratory contaminants (acetone, methylene chloride, 2-butanone, and sometimes freon) present in the trip blank? List compounds present with concentration and associated samples and apply the following rule. If sample concentration is ≤ 10x the blank value, assign a "B". If sample concentration is > 10x the blank value, no flag is necessary	
12.6	Yes	No	N/A	Are target analytes present in the trip blank? List compounds present with concentration and associated samples and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	

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13.0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables, reviewer will initial and date tables. A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e.g. internal use only). This narrative will address all qualifiers associated with each method.

	Data Usable With Qualification
J	Estimated quantitation based upon QC data
B	Estimated quantitation: possibly biased high or false positive based upon blank data
	Unusable Data
R	Data rejected based upon QC data
	Flagging Hierarchy
	R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Organic Data Review, 1994".
USACE "Shell for Analytical Chemistry Requirements", 1 February 2001.

Initial Review by:_____Date:_____
Senior Review by:_____Date:_____

SDG#_____
Matrix_____

SUPPLEMENTAL NOTES

Section Heading

DQE SW-846 Method 8270C Rev. 07/20/04
(BNA – Semi -Volatile Organic Compounds)

Initial Review by:_____ Date:_____
Senior Review by:_____ Date:_____

SDG#_____
Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
SW-846 8270C
(Semi-volatiles)

Note: The following Data Quality Evaluation (DQE) Standard Operating Procedure (SOP) for SW-846 8270C (semi-volatiles) incorporates the procedures outlined in the COE Shell Document (USACE, 2001). Be aware that Method 8270C strictly limits GC/MS analytical time to a 12 hour window following a successful tune. Table 1-7 of the COE Shell Document (USACE, 2001) is the summary of Method 8270C quality objectives. In lieu of copying materials from the SDG that are outside of the following QA/QC criteria, record the sequential page number/s provided on the bottom right hand corner of the SDG in the space provided to the right of the question.

1.0 SDG Batch Information and Sample Integrity

					Notes
1.1	Yes ___	No ___	N/A ___	Was the method specific 7 day holding time met for semi-volatiles extraction of water samples? Holding time is calculated as time elapsed from sampling to analysis. If holding time is exceeded by twice the allotted time, qualify the data as unusable and flag results R. If holding time is exceeded in less than twice the allotted time, flag results J.	
1.2	Yes ___	No ___	N/A ___	Was the method specific 40 day holding time met for semi-volatiles analysis of the extract? Holding time is calculated as time elapsed from extraction end date to analysis date. If holding time is exceeded by twice the allotted time, qualify the data as unusable and flag results R. If holding time is exceeded in less than twice the allotted time, flag results J.	
1.2.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of semi-volatiles water samples? [1 liter amber glass bottles with Teflon lined caps, no preservative @ 4° C]	
1.2.2	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to semi-volatiles data results and proceed to next method in SDG.**	
1.3	Yes ___	No ___	N/A ___	Was the correct method used for analysis of semi-volatiles? [SW-846: Water Prep Method 3510C or 3520C/Analysis Method 8270C]	

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2.0 GC/MS Instrument Performance Check (Tune)

					Notes
2.1	Yes	No	N/A	Did the laboratory include the GC/MS tuning and mass calibration summary forms performed with 50 ng/ul decafluorotriphenylphosphine (DFTPP) for the initial calibration and each daily 12 hour sequence? Note SDG page number/s.	
2.2	Yes	No	N/A	Did the tune/s pass the criteria as established in Method 8270C? Verify that the tuning criteria listed on the lab's form matches that of the method as follows:	

m/z	Required Intensity (relative abundance)
51	30 to 60% of m/z 198
68	< 2% of m/z 69
70	< 2% of m/z 69
127	40 to 60% of m/z 198
197	< 1% of m/z 198
198	Base Peak, 100% relative abundance
199	5 to 9% of mass 198
275	10 to 30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17 to 23% of mass 442

If tune criteria failed, qualify the associated sample data as unusable and flag R.

3.0 Initial Calibration

3.1	Yes	No	N/A	Are the Initial Calibration forms present with at least 5 calibration levels for semi-volatiles? If less than 5 standards were used, qualify the associated sample data as unusable and flag R Record SDG page number/s	
3.2	Yes	No	N/A	If a quadratic curve was used for any compound, have at least 6 standards been analyzed and included in the calibration of that compound? If less than 6 standards were used, qualify the associated sample data as unusable and flag R.	

Notes

3.3 Yes ___ No ___ N/A ___

Do the System Performance Check Compounds (SPCCs) meet the minimum Response Factor (RF) values per method requirements? The minimum mean response factor for the semi-volatile SPCCs is 0.050 for N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, and 4-nitrophenol.
If SPCC compounds exhibit a mean RF less than 0.050, qualify ***all*** associated sample SVOC results as unusable and flag "R".

3.4 Yes ___ No ___ N/A ___

Is the RSD for each individual Calibration Check Compound (CCC) less than or equal to 30%? The CCCs are:

Base/Neutral Fraction	Acid Fraction
1,4-dichlorobenzene	phenol
hexachlorobutadiene	2-nitrophenol
Acenaphthene	2,4-dichlorophenol
diphenylamine	4-chloro-3-methylphenol
fluoranthene	2,4,6-trichlorophenol
di-n-octyl phthalate	pentachlorophenol
benzo(a)pyrene	

If CCCs exceed 30% RSD, qualify *all* associated sample SVOC results as unusable and flag R.

3.5 Yes ___ No ___ N/A ___

All other target analytes: If Average Response Factor (RF) was used, is the RSD ≤ 15% or if a linear regression was used, is the initial calibration correlation coefficient (r) ≥ 0.995 ($r^2 \geq 0.990$)? Alternately, the mean %RSD for all target analytes must be ≤ 15%, with no target analyte exceeding 40% RSD. See Section 1.4 of Method 8270C for a discussion of analytes that typically require special treatment. Qualify compounds with a % RSD greater than 40 as unusable and flag R.

3.6 Yes ___ No ___ N/A ___

Was an alternate source Initial Calibration Verification (ICV) check standard analyzed at the completion of a valid Initial Calibration? This standard is typically prepared at a concentration in the middle of the calibration range. Record SDG page number/s.

3.7 Yes ___ No ___ N/A ___

Was the alternate source ICV within ± 30% of the true value? If a compound exceeds 30%, evaluate if this compound is an analyte of interest. If it is, check the recovery in the LCS. If both are outside recovery limits, flag that compound as unusable (R) in that 12 hour sequence. If only the ICV exceeds recovery criteria, then flag that compound in the 12 hour sequence as estimated (J or UJ).

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Initial Review by:_____Date:_____
Senior Review by:_____Date:_____

SDG#_____
Matrix_____

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4.0 Continuing Calibration

					Notes
4.1	Yes	No	N/A	Was a Continuing Calibration Verification (CCV) analyzed at the beginning of each 12 hour sequence, before the analysis of samples?	
4.2	Yes	No	N/A	Are the Continuing Calibration Verification (CCV) forms present? Record SDG page number/s.	
4.3	Yes	No	N/A	Do the System Performance Check Compounds (SPCCs) meet the minimum Response Factor (RF) values in the CCV per method requirements? The minimum response factor for the semi-volatile SPCCs is 0.05 for 2,4-dinitrophenol, N-nitrosodi-n-propylamine, hexachlorocyclopentadiene, and 4-nitrophenol. If SPCC compounds exhibit a mean RF less than 0.050, qualify *all* associated sample SVOC results as unusable and flag R.	
4.4	Yes	No	N/A	Is the %D for each individual Calibration Check Compound (CCC) less than or equal to 30%? The CCCs are:	
4.5	Yes	No	N/A	Are the remaining target analytes within 20%D if average RF is used or ± 20% drift if a linear or quadratic calibration is used? If a compound exceeds 20%D or drift, evaluate if this compound is an analyte of interest. If it is, check the recovery in the LCS. If both are outside recovery limits, flag that compound as rejected (R) in that 12 hour sequence If only the CCV exceeds recovery criteria, then flag that compound in the 12 hour sequence as estimated (J).	

Base/Neutral Fraction	Acid Fraction
1,4-dichlorobenzene	phenol
hexachlorobutadiene	2-nitrophenol
Acenaphthene	2,4-dichlorophenol
diphenylamine	4-chloro-3-methylphenol
fluoranthene	2,4,6-trichlorophenol
di-n-octyl phthalate	pentachlorophenol
benzo(a)pyrene	

If CCCs exceed 30% RSD, qualify *all* associated sample SVOC results as unusable and flag R

5.0 Method Blanks

					Notes
5.1	Yes ___	No ___	N/A ___	Is a Method Blank summary present for each blank prepared and analyzed? Record SDG page number/s.	
5.2	Yes ___	No ___	N/A ___	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix?	
5.3	Yes ___	No ___	N/A ___	Are the common laboratory contaminants (phthalates) less than the PQL/RL in each method blank? If not, did the lab re-extract and/or reanalyze the blank or associated samples? List compounds present with concentration and apply the following rule. If not present in any field samples, then no flag is required. Refer to Method Blank Report (Form I). If sample concentration is < 10x the blank value, assign a "B" If sample concentration is > 10x the blank value, no flag is necessary	
5.4	Yes ___	No ___	N/A ___	Are target analytes less than one-half the RL in the method blank? Or, less than 5% of the regulatory limit associated with that analyte, or less than 5% of the sample result for the same analyte, whichever is greater for the method blank to be acceptable If not, did the lab re-extract and/or reanalyze the blank or associated samples? List compounds present with concentration and apply the following rule. If not found in any field samples, then no flag is required. If sample concentration is < 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	

6.0 Laboratory Control Standard

6.1	Yes ___	No ___	N/A ___	Is the LCS and/or LCS duplicate summary form present for each matrix or every 20 samples? Record SDG page number/s.	
6.2	Yes ___	No ___	N/A ___	Was a Laboratory Control Standard (LCS) analyzed with each SDG or every 20 samples of similar matrix? If no LCS was analyzed, qualify ***all*** associated SVOC sample results as estimated and flag "J".	

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Notes

6.3 Yes ___ No ___ N/A ___

LCS/LCSD spike recoveries for 8270C vary by stability of compounds. Generally, the PAH and phthalates are very stable and constitute approximately 25% of the compounds spiked. Conversely, the amines, phenols and acids in general are poor performers and also constitute approximately 25% of the compounds spiked. The COE has decided based on historical and ongoing data collection, that recoveries fall into the following pattern for **water**. Stable compounds (~25%) should recover in the 60-120% range, while 50% of the spiked compounds should recover within 45-135%. The poor performers (~25%) should recover within 20-150%. With at least 78 spiked compounds, up to 5 failures are allowed under the Sporadic Marginal Failure limits of 15-150%.
See Table I-15 of the COE Shell document for guidance if less than 78 compounds are present.
If a LCS and LCSD were analyzed, flag results if **both LCS and LCSD recoveries are outside QC limits*
*Flag Criteria.
Hits in sample that fail high in the LCS = J
Hits and NDs that fail low in the LCS = J

7.0 Internal Standards and Surrogates

7.1 Yes ___ No ___ N/A ___

Are the Internal standard summary forms present? Record SDG page number/s.

7.2 Yes ___ No ___ N/A ___

Were the Internal Standard area counts from each standard, sample and blank within 2 times (–50% to +100%) that found in the mid-point standard of the most recent initial calibration? If not, flag associated compound results of the affected IS "J". However, if IS area counts exceed 50% of the lower limit, qualify sample results as unusable and flag R.

7.3 Yes ___ No ___ N/A ___

Were the Internal Standard retention times from each standard, sample and blank within 30 seconds of the retention time found in the mid-point standard of the most recent initial calibration? If IS retention times exceed limits, qualify sample results as unusable and flag R.

7.4	Yes ___	No ___	N/A ___	Are the Surrogate recovery summary forms present? Record SDG page number/s.	
7.5	Yes ___	No ___	N/A ___	Were the Surrogate Standards in interference-free matrix (e.g. Method Blank and LCS) within the following limits: Water: B/N compounds – 60-120%; Acid compounds – 45-135%. Only **1** Sporadic Marginal Failure is allowed in each fraction (BN and A) with the following criteria: **Water:** 15-150% These matrices are considered the lab QC samples such as the method blanks, and LCSs and field QC samples such as trip blanks and rinsate blanks. Corrective action by the laboratory should be reanalysis of the blank or LCS followed by re-extraction if failure is confirmed. If method blank and LCS surrogate standards fail USACE limits, but are within *laboratory-established* limits, no flags are applied. However, if both the USACE and *laboratory-established* limits are exceeded **and** surrogate recoveries in the associated samples exceed limits, qualify associated sample results J. If surrogate recovery exceeds SMF limits, qualify the associated fraction as unusable and flag results R.	**Notes**
7.6	Yes ___	No ___	N/A ___	Were the Surrogate Standards in project sample matrix within the following limits: Water: B/N compounds – 45-135%; Acid compounds – 35-140%. Only **1** Sporadic Marginal Failure is allowed with the following criteria: **Water:** 15-150% Corrective action by the laboratory should be reanalysis of the sample followed by re-extraction if failure is confirmed. If surrogate recovery exceeds USACE limits but are above the SMF limits, qualify associated sample fraction results J. If surrogate recovery exceeds SMF limits, qualify the associated fraction as unusable and flag results R.	

8.0 Matrix Spikes

8.1	Yes ___	No ___	N/A ___	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Record SDG page number/s.	
8.2	Yes ___	No ___	N/A ___	Were MS/MSDs analyzed at a frequency of 1 per 20 samples and if designated by project team, were proper samples spiked? If not, list spiked samples and indicate if they are project samples or not.	

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Notes

8.3 Yes ___ No ___ N/A ___

Were the recoveries of the MS/MSD within COE limits of 45-135% for water? If a full list of 78 compounds is being spiked, then 5 failures are allowed within the Sporadic Marginal Failure limits: 15-150% for water as prescribed in the COE Shell document, Table I-7. See Table I-15 of the COE Shell document for guidance if less than 78 compounds are present. Reference SDG page number/s. If ***both*** recoveries exceed USACE limits but are within the SMF limits, qualify associated sample results J. If ***both*** recoveries exceed SMF limits, qualify the associated sample results as unusable and flag results R.

NOTE: $\%R = \frac{(SSR-SR)}{SA} \times 100$

Where, %R = Percent spike recovery
SSR = Spiked sample result
SR = Sample result
SA = Spike added

NOTE: Control limits apply only when spike sample results fall within the normal calibration range. If dilutions are required due to high sample concentrations, the data are evaluated but no flags are applied.

8.4 Yes ___ No ___ N/A ___

Was the RPD between the MS/MSD < 50% for water? RPD for solids should not exceed 60%. If a full list of 78 compounds is being spiked, then 5 failures are allowed within the Sporadic Marginal Failure limits (RPD less than or equal to 60%), as prescribed in the COE Shell document, Table I-7. See Table I-15 of the COE Shell document for guidance if less than 78 compounds are spiked. If RPD exceeds USACE limits but is above the SMF limits, qualify associated sample results J. If RPD exceeds SMF limits, qualify the associated sample results as unusable and flag results R.

NOTE: $RPD = \frac{S-D}{(S+D)/2} \times 100$

Where, S = MS sample result
D = MSD sample result

9.0 Duplicates

					Notes
9.1	Yes ___	No ___	N/A ___	Were any intra-laboratory samples or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC. Record and cross-reference sample ID along with SDG page number/s.	
9.2	Yes ___	No ___	N/A ___	Is the RPD between compounds present in the sample and duplicate ≤ 50% for water? If not, list sample ID, concentration of both samples and RPDs. For RPDs that exceed these limits, flag the compound as estimated (J) in both samples.	

10.0 Compound Quantitation and Reported Detection Limits

10.1	Yes ___	No ___	N/A ___	Are results present for all samples sent to the lab for semi-volatiles?	
10.2	Yes ___	No ___	N/A ___	Have PQLs been adjusted to properly reflect sample dilutions and/or percent moisture?	
10.3	Yes ___	No ___	N/A ___	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis.	
10.4	Yes ___	No ___	N/A ___	Were any samples re-extracted for any reason? If so, record sample number and brief description of the reason for re-extraction.	

11.0 Field QA/QC

11.1	Yes ___	No ___	N/A ___	Were any rinsate blanks collected? If so, identify the rinsate and the associated samples.	
11.2	Yes ___	No ___	N/A ___	Are the common laboratory contaminants (phthalates) present in the rinsate blank? List compounds present with concentration and apply the following rule. If sample concentration is < 10x the blank value, assign a "B". If sample concentration is > 10x the blank value, no flag is necessary	

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Notes

11 3 Yes ___ No ___ N/A ___ Are target analytes present in the rinsate blank? List compounds present with concentration and apply the following rule. If not found in any field samples, then no flag is required.
If sample concentration is < 5x the blank value, assign a "B".
If sample concentration is > 5x the blank value, no flag is necessary

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12 0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables, reviewer will initial and date tables. A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e.g. internal use only). This narrative will address all qualifiers associated with each method.

Data Usable With Qualification

J	Estimated quantitation based upon QC data
B	Estimated quantitation: possibly biased high or false positive based upon blank data

Unusable Data

R	Data rejected based upon QC data

Flagging Hierarchy

R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Organic Data Review, 1994".
USACE "Shell for Analytical Chemistry Requirements", 1 February 2001

Initial Review by:_____Date:_____
Senior Review by:_____Date:_____

SDG#_____
Matrix_____

SUPPLEMENTAL NOTES

Section Heading

8772249

Initial Review by:_____ Date _____ SDG#_____
Senior Review by:_____ Date:_____ Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
SW-846 8081A
(Chlorinated Pesticides)

Note: The following Data Quality Evaluation (DQE) for SW-846 8081A (Chlorinated Pesticides) as performed by Severn Trent Laboratory – North Canton will be evaluated according to the COE Shell Document. Table I4 of the COE Shell Document is the summary of Method 8081A quality objectives. In lieu of copying materials from the SDG that are outside of the following QA/QC criteria, record the sequential page number/s provided on the bottom right hand corner of the SDG in the space provided to the right of the question.

1.0 Sample Integrity

					Notes
1.1	Yes ___	No ___	N/A ___	Was the method specific 7 day extraction holding time and 40 day analysis holding time met for pesticides in water (14 days extraction holding time/40 day analysis holding time for pesticides in soil)? Holding time is calculated as time elapsed from sampling to analysis. If not, flag results J.	
1.1.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of pesticide sample? [Water: 2 x 1 Liter amber glass bottles, @ 4° C Soil: 1 x 8 or 16 oz wide-mouth glass jar, @ 4° C]	
1.1 2	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to pesticide data results and proceed to next method in SDG.**	

2 0 Laboratory Method

2.1	Yes ___	No ___	N/A ___	Was the correct method used for analysis of pesticides? [SW-846: Water Prep Method 3520C/Analysis Method 8081A] [SW-846· Soil Prep Method 3550B/Analysis Method 8081A] NOTE: Samples may undergo several cleanup procedures by methods 3620B (Florisil Column Cleanup), 3660B (Sulfur Cleanup), and 3640A (Gel Permeation Cleanup).	
2.2	Yes ___	No ___	N/A ___	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL. Results reported between the MDL and PQL are flagged J.	

3 0 Breakdown (Injection Port Inertness Check)

					Notes
3 1	Yes	No	N/A	Was column breakdown for endrin and DDT assessed each day prior to analysis on each instrument used for the pesticide analysis? Record SDG page numbers. ACTION: If no, reject (R) positive results for endrin, endrin ketone, endrin aldehyde, 4,4'-DDT, 4,4'-DDD, and 4,4'-DDE.	
3.2	Yes	No	N/A	Is the % degradation of either endrin or DDT ≥ 15% ? NOTE: %Breakdown DDT = Amount found (ng) (DDD+DDE) x 100 / Amount (ng) of DDT injected NOTE: %Breakdown Endrin = Amount found (ng) endrin aldehyde+endrin ketone x 100 / Amount (ng) of endrin injected ACTION: If DDT breakdown is greater than 15%, qualify positive results for DDT, DDE, and DDD as estimated (J). If endrin breakdown exceeds 15%, qualify positive results for endrin, endrin aldehyde, and endrin ketone as estimated (J).	

4.0 Initial Calibration

4.1	Yes	No	N/A	Are the Initial Calibration forms present with at least 5 calibration levels for pesticides on both the primary and secondary columns? Record SDG page numbers.	
4.2	Yes	No	N/A	If a quadratic curve was used for any compound, have at least 6 standards been analyzed and included in the calibration of that compound?	

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Initial Review by:_____ Date:_____ SDG#_____
Senior Review by:_____ Date:_____ Matrix_____

					Notes
4.3	Yes	No	N/A	If Average Response Factor (RF) for all other target analytes was used, is the RSD ≤ 20% **or** if a linear regression was used, is the initial calibration correlation coefficient (r) ≥ 0.995 (r^2 ≥ 0.990)? Alternately, the mean %RSD for all target analytes must be ≤ 20%, with no target analyte exceeding 40%RSD. If not, flag associated sample results R.	
4.4	Yes	No	N/A	Was an alternate source Initial Calibration Verification (ICV) check standard analyzed at the completion of a valid Initial Calibration? This standard is typically prepared at a concentration in the middle of the calibration range. Record SDG page numbers.	
4.5	Yes	No	N/A	Was the alternate source ICV within 85-115% of the true value? If not, flag results J.	

5.0 Continuing Calibration

5.1	Yes	No	N/A	Was a Continuing Calibration Verification (CCV) analyzed at the beginning and end of each sequence, before and after the analysis of samples?	
5.2	Yes	No	N/A	Are the Continuing Calibration Verification (CCV) forms present? Record SDG page numbers and associated samples.	
5.3	Yes	No	N/A	Are the target analytes within 15%D if average RF is used or ± 15% drift if a linear or quadratic calibration is used or is the average % drift or % D for all target analytes within ± 15%? If a compound exceeds 15%D or drift, evaluate if this compound is an analyte of interest. If the CCV exceeds recovery criteria and is less than 30% D or drift, then flag that compound in the sequence as estimated (J). Any compound greater than 30%D or drift should be rejected (R) in that sequence. *NOTE: Closing CCV per section 7.5.7 of SW 8081A* *"However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e. >15%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present."*	

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6 0 Method Blanks

					Notes
6.1	Yes	No	N/A	Is the Method Blank summary present? Record SDG page numbers and associated samples.	
6.2	Yes	No	N/A	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix in each analytical sequence?	
6 3	Yes	No	N/A	Are all analytes less than the PQL in the method blank? List compounds present with concentration and apply the following rule. If sample concentration is < 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	

7.0 Laboratory Control Standard

7 1	Yes	No	N/A	Is the Laboratory Control Standard (LCS) and/or LCS duplicate summary form present? Record SDG page numbers and associated samples	
7 2	Yes	No	N/A	Was an LCS analyzed with each SDG or every 20 samples of similar matrix within each sequence?	
7 3	Yes	No	N/A	For waters and soils, are spiked recoveries within 50-130% in the LCS/LCSD? If a full list of 21 compounds is being analyzed, then 2 SMFs are allowed at 30-150%, as prescribed in the COE Shell document, Table I4. If the LCS/LCSD includes a subset of compounds then 1 SMF is allowed. Only flag if **both** LCS and LCSD recoveries are outside QC limits. Flag Criteria: Hits in sample that fail high in the LCS = J Hits and NDs that fail low in the LCS = J	

8.0 Matrix Spikes

8.1	Yes	No	N/A	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Record SDG page numbers.	
8.2	Yes	No	N/A	Were Matrix Spike/Matrix Spike Duplicate (MS/MSD) analyzed at a frequency of 1 per 20 samples as designated by project team? List samples that were spiked	

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					Notes
8.3	Yes	No	N/A	Were the recoveries of the MS/MSD within COE limits of 40-140% for water or soil? Reference SDG page number. If a full list of 21 compounds is being analyzed, then 2 SMFs are allowed at 30-150%, as prescribed in the COE Shell document, Table 14. If the MS includes a subset of compounds then 1 SMF is allowed. If recoveries are high, flag positive results in the parent sample "J". If recoveries are low, flag positive and non-detect results in the parent sample "J". NOTE: Control limits apply only when spike sample results fall within the normal calibration range. If dilutions are required due to high sample concentrations, the data are evaluated but no flags are applied.	
8.4	Yes	No	N/A	Was the RPD between the MS/MSD < 50% for water or soil? If a full list of 21 compounds is being analyzed, then 2 SMFs are allowed at RPD ≤ 60%, as prescribed in the COE Shell document, Table 14. If the MS includes a subset of compounds then 1 SMF is allowed. If not, flag results J.	

9.0 Duplicates

9.1	Yes	No	N/A	Were any intra-laboratory sample or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC. Record and cross-reference sample ID along with SDG page numbers.	
9.2	Yes	No	N/A	Is the RPD between compounds present in the sample and duplicate ≤ 50%? If not, list sample ID, concentration of both samples, RPD and SDG page number/s. For RPDs that exceed 50%, flag the compound with as estimated (J) in both samples.	

10.0 Surrogates

10.1	Yes	No	N/A	Are the Surrogate standard summary forms present? Record SDG page numbers.	
10.2	Yes	No	N/A	Were the Surrogate Standards from each standard, sample and blank within 50-130% recovery in "interference free" water or soil matrices? These matrices are considered the lab QC samples such as the method blanks, LCSs, CCVs, etc. Corrective action by the laboratory for surrogate failures should be reanalysis of the sample.	

					Notes
10.3	Yes	No	N/A	Were the Surrogate Standards in "project sample matrix" within 40-140% recovery? No allowance for Sporadic Marginal Failures listed in Table 14 of the COE Shell Document. **Corrective action by the laboratory for surrogate failures should be reanalysis of the sample.** If not, flag positive results J for recoveries above 140% and flag positive and non-detect results J for recoveries below 40%.	

11.0 Compound Quantitation, Reported Detection Limits and Confirmation

11.1	Yes	No	N/A	Are results present for all samples sent to the lab for pesticides?	
11.2	Yes	No	N/A	Have PQLs been adjusted to properly reflect sample dilutions?	
11.3	Yes	No	N/A	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis	
11.4	Yes	No	N/A	Was the analyte confirmed on a second column? Was it confirmed within a 40% RPD between sample results? **NOTE**: Confirmation is necessary for results at or above the PQL. Report primary column results unless interferences are present on the primary column, in which case the confirmation result can be reported. ACTION: If compound was not detected on the second column, the positive result should not be reported. If the RPD was > 40%, the value should be reported with a (J) qualifier.	

12.0 Field QA/QC

12.1	Yes	No	N/A	Were any rinsate blanks collected?	
12.2	Yes	No	N/A	Are pesticides present in the rinsate blank? List compounds present with concentration and apply the following rule. If sample concentration is < 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	

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13 0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables, reviewer will initial and date tables. A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e g. internal use only). This narrative will address all qualifiers associated with each method.

	Data Usable With Qualification
J	Estimated quantitation based upon QC data
B	Estimated quantitation· possibly biased high or false positive based upon blank data
	Unusable Data
R	Data rejected based upon QC data
	Flagging Hierarchy
	R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Organic Data Review, 1994".
USACE "Shell for Analytical Chemistry Requirements", 1 February 2001.

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SUPPLEMENTAL NOTES

Section Heading

DQE SW-846 Method 8082 07/27/04
(PCBs)

Initial Review by:_____ Date:_____ SDG#_____
Senior Review by _____ Date:_____ Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
SW-846 8082
(Polychlorinated Biphenyls)

8772258

Note: The following Data Quality Evaluation (DQE) for SW-846 8082 (Polychlorinated Biphenyls) as performed by Severn Trent Laboratory – North Canton will be evaluated according to the COE Shell Document. Table 15 of the COE Shell Document is the summary of Method 8081A quality objectives. In lieu of copying materials from the SDG that are outside of the following QA/QC criteria, record the sequential page number/s provided on the bottom right hand corner of the SDG in the space provided to the right of the question.

					Notes
1.0 Sample Integrity					
1.1	Yes ___	No ___	N/A ___	Was the method specific 7 day extraction holding time and 40 day analysis holding time met for PCBs in water (14 days extraction holding time/40 day analysis holding time for PCBs in soil)? Holding time is calculated as time elapsed from sampling to analysis If not, flag results J.	
1.1.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of PCB samples? [Water 2 x 1 Liter amber glass bottles, @ 4° C Soil: 1 x 8 or 16 oz wide-mouth glass jar, @ 4° C]	
1.1.2	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to PCB data results and proceed to next method in SDG.**	
2.0 Laboratory Method					
2.1	Yes ___	No ___	N/A ___	Was the correct method used for analysis of PCBs? [SW-846: Water Prep Method 3520C/Analysis Method 8082] [SW-846: Soil Prep Method 3550B/Analysis Method 8082] NOTE: Samples may undergo several cleanup procedures by methods 3620B (Florisil Column Cleanup), 3660B (Sulfur Cleanup), and 3640A (Gel Permeation Cleanup).	
2.2	Yes ___	No ___	N/A ___	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL. Results reported between the MDL and PQL are flagged J.	

3.0 Initial Calibration

					Notes
3.1	Yes ___	No ___	N/A ___	Are the Initial Calibration forms present with at least 5 calibration levels for pesticides on both the primary and secondary columns? Record SDG page numbers.	
3.2	Yes ___	No ___	N/A ___	If a quadratic curve was used for any compound, have at least 6 standards been analyzed and included in the calibration of that compound?	
3.3	Yes ___	No ___	N/A ___	If Average Response Factor (RF) for all other target analytes was used, is the RSD ≤ 20% **or** if a linear regression was used, is the initial calibration correlation coefficient (r) ≥ 0.995 (r^2 ≥ 0.990)? Alternately, the mean %RSD for all target analytes must be ≤ 20%, with no target analyte exceeding 40%RSD. If not, flag associated sample results R.	
3.4	Yes ___	No ___	N/A ___	Was an alternate source Initial Calibration Verification (ICV) check standard analyzed at the completion of a valid Initial Calibration? This standard is typically prepared at a concentration in the middle of the calibration range. Record SDG page numbers.	
3.5	Yes ___	No ___	N/A ___	Was the alternate source ICV within 85-115% of the true value? If not, flag results J.	

4.0 Continuing Calibration

4.1	Yes ___	No ___	N/A ___	Was a Continuing Calibration Verification (CCV) analyzed at the beginning and end of each sequence, before and after the analysis of samples?	
4.2	Yes ___	No ___	N/A ___	Are the CCV forms present? Record SDG page numbers and associated samples.	

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Notes

4.3 Yes ___ No ___ N/A ___ Are the target analytes within 15%D if average RF is used or ± 15% drift if a linear or quadratic calibration is used or is the average % drift or % D for all target analytes within ± 15%? If a compound exceeds 15%D or drift, evaluate if this compound is an analyte of interest. If the CCV exceeds recovery criteria and is less than 30% D or drift, then flag that compound in the sequence as estimated (J). Any compound greater than 30%D or drift should be rejected (R) in that sequence.

5.0 Method Blanks

5.1 Yes ___ No ___ N/A ___ Is the Method Blank summary present? Record SDG page numbers and associated samples.

5.2 Yes ___ No ___ N/A ___ Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix in each analytical sequence?

5.3 Yes ___ No ___ N/A ___ Are all analytes less than the PQL in the method blank? List compounds present with concentration and apply the following rule.
If sample concentration is < 5x the blank value, assign a "B".
If sample concentration is > 5x the blank value, no flag is necessary

6.0 Laboratory Control Standard

6.1 Yes ___ No ___ N/A ___ Is the Laboratory Control Standard (LCS) and/or LCS duplicate summary form present? Record SDG page numbers and associated samples.

6.2 Yes ___ No ___ N/A ___ Was an LCS analyzed with each SDG or every 20 samples of similar matrix within each sequence?

6.3 Yes ___ No ___ N/A ___ For waters and soils, are spiked recoveries within 50-130% in the LCS/LCSD? Only flag if **both** LCS and LCSD recoveries are outside QC limits.
Flag Criteria:
Hits in sample that fail high in the LCS = J
Hits and NDs that fail low in the LCS = J

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Initial Review by:_____Date:_____ SDG#_____
Senior Review by:_____Date:_____ Matrix_____

7.0 Matrix Spikes

					Notes
7.1	Yes ___	No ___	N/A ___	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Record SDG page numbers.	
7.2	Yes ___	No ___	N/A ___	Were MS/MSDs analyzed at a frequency of 1 per 20 samples as designated by project team? List samples that were spiked.	
7.3	Yes ___	No ___	N/A ___	Were the recoveries of the MS/MSD within COE limits of 40-140% for water or soil? Reference SDG page number. If recoveries are high, flag positive results in the parent sample "J" If recoveries are low, flag positive and non-detect results in the parent sample "J". NOTE: Control limits apply only when spike sample results fall within the normal calibration range. If dilutions are required due to high sample concentrations, the data are evaluated but no flags are applied.	
7.4	Yes ___	No ___	N/A ___	Was the RPD between the MS/MSD < 50% for water or soil? If not, flag results J.	

8.0 Duplicates

8.1	Yes ___	No ___	N/A ___	Were any intra-laboratory sample or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC. Record and cross-reference sample ID along with SDG page numbers.	
8.2	Yes ___	No ___	N/A ___	Is the RPD between compounds present in the sample and duplicate ≤ 50%? If not, list sample ID, concentration of both samples, RPD and SDG page number/s. For RPDs that exceed 50%, flag the compound with as estimated (J) in both samples.	

9.0 Surrogates

9.1	Yes ___	No ___	N/A ___	Are the Surrogate standard summary forms present? Record SDG page numbers.	
9.2	Yes ___	No ___	N/A ___	Were the Surrogate Standards from each standard, sample and blank within 50-130% recovery in "interference free" water or soil matrices? These matrices are considered the lab QC samples such as the method blanks, LCSs, CCVs, etc. Corrective action by the laboratory for surrogate failures should be reanalysis of the sample.	

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					Notes
9.3	Yes	No	N/A	Were the Surrogate Standards in "project sample matrix" within 40-140% recovery? No allowance for Sporadic Marginal Failures listed in Table 15 of the COE Shell Document. **Corrective action by the laboratory for surrogate failures should be reanalysis of the sample.** If not, flag positive results J for recoveries above 140% and flag positive and non-detect results J for recoveries below 40%.	

10.0 Compound Quantitation, Reported Detection Limits and Confirmation

10.1	Yes	No	N/A	Are results present for all samples sent to the lab for PCBs?	
10.2	Yes	No	N/A	Have PQLs been adjusted to properly reflect sample dilutions?	
10.3	Yes	No	N/A	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis.	
10.4	Yes	No	N/A	Was the analyte confirmed on a second column? Was it confirmed within a 40% RPD between sample results? **NOTE**: Confirmation is necessary for results at or above the PQL. Report primary column results unless interferences are present on the primary column, in which case the confirmation result can be reported. ACTION: If compound was not detected on the second column, the positive result should not be reported If the RPD was > 40%, the value should be reported with a (J) qualifier.	

11.0 Field QA/QC

11.1	Yes	No	N/A	Were any rinsate blanks collected?	
11.2	Yes	No	N/A	Are pesticides present in the rinsate blank? List compounds present with concentration and apply the following rule. If sample concentration is < 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	

12.0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables. reviewer will initial and date tables. A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e.g. internal use only) This narrative will address all qualifiers associated with each method.

	Data Usable With Qualification
J	Estimated quantitation based upon QC data
B	Estimated quantitation: possibly biased high or false positive based upon blank data
	Unusable Data
R	Data rejected based upon QC data
	Flagging Hierarchy
	R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Organic Data Review, 1994".
USACE "Shell for Analytical Chemistry Requirements", 1 February 2001.

Initial Review by:_____Date:_____ SDG#_____
Senior Review by:_____Date:_____ Matrix_____

SUPPLEMENTAL NOTES

Section Heading

Initial Review by:_____Date:_____ SDG#_____
Senior Review by:_____Date:_____ Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
SW-846 8151A
(Herbicides)

Note: The following Data Quality Evaluation (DQE) for SW-846 8151A (Herbicides) as performed by Severn Trent Laboratory – North Canton will be evaluated according to the labs QA/QC program. The COE Shell Document does not specifically address herbicides analysis.

1.0 Sample Integrity

					Notes
1.1	Yes ___	No ___	N/A ___	Was the method specific 7 day extraction holding time and 40 day analysis holding time met for herbicides in water (14 days extraction holding time/40 day analysis holding time for herbicides in soil)? Holding time is calculated as time elapsed from sampling to analysis. If not, flag results J.	
1.1.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of herbicide sample? [Water: 2 x 1 Liter amber glass bottles, @ 4° C Soil: 1 x 8 or 16 oz wide-mouth glass jar, @ 4° C]	
1.1.2	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to herbicide data results and proceed to next method in SDG.**	

2.0 Laboratory Method

2.1	Yes ___	No ___	N/A ___	Was the correct method used for analysis of herbicides? [SW-846 Water Prep Method 3520C/Analysis Method 8151A] [SW-846: Soil Prep Method 3550B/Analysis Method 8151A] NOTE: Samples may undergo several cleanup procedures by methods 3620B (Florisil Column Cleanup), 3660B (Sulfur Cleanup), and 3640A (Gel Permeation Cleanup).	
2.2	Yes ___	No ___	N/A ___	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL. Results reported between the MDL and PQL are flagged J.	

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Initial Review by:_____ Date:_____ SDG#_____
Senior Review by:_____ Date:_____ Matrix_____

3.0 Initial Calibration

					Notes
3.1	Yes	No	N/A	Are the Initial Calibration forms present with at least 5 calibration levels for pesticides on both the primary and secondary columns? Record SDG page numbers.	
3.2	Yes	No	N/A	If a quadratic curve was used for any compound, have at least 6 standards been analyzed and included in the calibration of that compound?	
3.3	Yes	No	N/A	If Average Response Factor (RF) for all other target analytes was used, is the RSD ≤ 20% **or** if a linear regression was used, is the initial calibration correlation coefficient (r) ≥ 0.995 ($r^2 \geq 0.990$)? Alternately, the mean %RSD for all target analytes must be ≤ 20%, with no target analyte exceeding 40%RSD. If not, flag associated sample results R.	
3.4	Yes	No	N/A	Was an alternate source Initial Calibration Verification (ICV) check standard analyzed at the completion of a valid Initial Calibration? This standard is typically prepared at a concentration in the middle of the calibration range. Record SDG page numbers.	
3.5	Yes	No	N/A	Was the alternate source ICV within 85-115% of the true value? If not, flag results J.	

4.0 Continuing Calibration

4.1	Yes	No	N/A	Was a Continuing Calibration Verification (CCV) analyzed at the beginning and end of each sequence, before and after the analysis of samples?	
4.2	Yes	No	N/A	Are the CCV forms present? Record SDG page numbers and associated samples.	
4.3	Yes	No	N/A	Are the target analytes within 15%D if average RF is used or ± 15% drift if a linear or quadratic calibration is used or is the average % drift or % D for all target analytes within ± 15%? If a compound exceeds 15%D or drift, evaluate if this compound is an analyte of interest. If the CCV exceeds recovery criteria and is less than 30% D or drift, then flag that compound in the sequence as estimated (J). Any compound greater than 30%D or drift should be rejected (R) in that sequence.	

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Initial Review by:_____ Date:_____ SDG#_____
Senior Review by:_____ Date:_____ Matrix_____

5.0 Method Blanks

					Notes
5.1	Yes ___	No ___	N/A ___	Is the Method Blank summary present? Record SDG page numbers and associated samples.	
5.2	Yes ___	No ___	N/A ___	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix in each analytical sequence?	
5.3	Yes ___	No ___	N/A ___	Are all analytes less than the PQL in the method blank? List compounds present with concentration and apply the following rule. If sample concentration is < 5x the blank value, assign a "B" If sample concentration is > 5x the blank value, no flag is necessary	

6.0 Laboratory Control Standard

6.1	Yes ___	No ___	N/A ___	Is the Laboratory Control Standard (LCS) and/or LCS duplicate summary form present? Record SDG page numbers and associated samples.	
6.2	Yes ___	No ___	N/A ___	Was an LCS analyzed with each SDG or every 20 samples of similar matrix within each sequence?	
6.3	Yes ___	No ___	N/A ___	For waters and soils, are spiked recoveries within 50-130% in the LCS/LCSD? Only flag if **both** LCS and LCSD recoveries are outside QC limits. Flag Criteria: Hits in sample that fail high in the LCS = J Hits and NDs that fail low in the LCS = J	

7.0 Matrix Spikes

7.1	Yes ___	No ___	N/A ___	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Record SDG page numbers.	
7.2	Yes ___	No ___	N/A ___	Were MS/MSDs analyzed at a frequency of 1 per 20 samples as designated by project team? List samples that were spiked.	

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					Notes
7.3	Yes	No	N/A	Were the recoveries of the MS/MSD within laboratory limits? Reference SDG page number If recoveries are high, flag positive results in the parent sample "J" If recoveries are low, flag positive and non-detect results in the parent sample "J". NOTE: Control limits apply only when spike sample results fall within the normal calibration range. If dilutions are required due to high sample concentrations, the data are evaluated but no flags are applied.	
7.4	Yes	No	N/A	Was the RPD between the MS/MSD within laboratory limits? If not, flag results J	

8.0 Duplicates

8.1	Yes	No	N/A	Were any intra-laboratory sample or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC. Record and cross-reference sample ID along with SDG page numbers.	
8.2	Yes	No	N/A	Is the RPD between compounds present in the sample and duplicate ≤ 50%? If not, list sample ID, concentration of both samples, RPD and SDG page number/s. For RPDs that exceed 50%, flag the compound with as estimated (J) in both samples.	

9.0 Surrogates

9.1	Yes	No	N/A	Are the Surrogate standard summary forms present? Record SDG page numbers	
9.2	Yes	No	N/A	Were the Surrogate Standards within laboratory limits? **Corrective action by the laboratory for surrogate failures should be reanalysis of the sample.** If not, flag positive results J for recoveries above limits and flag positive and non-detect results J for recoveries below limits.	

10.0 Compound Quantitation, Reported Detection Limits and Confirmation

10.1	Yes	No	N/A	Are results present for all samples sent to the lab for herbicides?	
10.2	Yes	No	N/A	Have PQLs been adjusted to properly reflect sample dilutions?	

					Notes
10.3	Yes ___	No ___	N/A ___	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis.	
10.4	Yes ___	No ___	N/A ___	Was the analyte confirmed on a second column? Was it confirmed within a 40% RPD between sample results? **NOTE**: Confirmation is necessary for results at or above the PQL. Report primary column results unless interferences are present on the primary column, in which case the confirmation result can be reported. ACTION: If compound was not detected on the second column, the positive result should not be reported. If the RPD was > 40%, the value should be reported with a (J) qualifier.	

11.0 Field QA/QC

11.1	Yes ___	No ___	N/A ___	Were any rinsate blanks collected?	
11.2	Yes ___	No ___	N/A ___	Are pesticides present in the rinsate blank? List compounds present with concentration and apply the following rule. If sample concentration is < 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	

8772269

12.0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables, reviewer will initial and date tables A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e.g. internal use only). This narrative will address all qualifiers associated with each method.

	Data Usable With Qualification
J	Estimated quantitation based upon QC data
B	Estimated quantitation: possibly biased high or false positive based upon blank data
	Unusable Data
R	Data rejected based upon QC data
	Flagging Hierarchy
	R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Organic Data Review, 1994".
USACE "Shell for Analytical Chemistry Requirements", 1 February 2001.

8772270

SUPPLEMENTAL NOTES

Section Heading

DQE SW-846 7470A/7471A Rev. 09/21/04
(mercury)

Initial Review by: _____ Date._____ SDG#_____
Senior Review by:_____ Date:_____ Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
SW-846 7470A/7471A
(Mercury)

8772272

Note: The following Data Quality Evaluation (DQE) for SW-846 7470A/7471A (mercury) as performed by Severn Trent Laboratories – North Canton, OH will be evaluated according to the QA/QC program outlined in the US Army Corp of Engineers Shell Document. In cases where data does not meet criteria, record the SDG page number for reference in lieu of copying. This checklist is not intended to be all encompassing and assumes personnel utilizing these forms are knowledgeable in data review. If at any time there is a questionable issue, consult the senior chemist.

1.0 Sample Integrity

					Notes
1.1	Yes ___	No ___	N/A ___	Were all samples sent to laboratory for dissolved metals analysis filtered before preservation? See the field Daily Quality Control Report (DQCR), field logs and/or sampling personnel for this information. If extenuating circumstances did not allow for filtering, list samples affected.	
1.2	Yes ___	No ___	N/A ___	Was the 28 day holding time met for mercury? Holding time is calculated as time elapsed from sampling to analysis. If not, flag results J.	
1.2.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of mercury samples? [water: 1 liter plastic with HNO_3 to pH<2 @ 4° C; soil: 8 oz. soil jar]	
1.2.2	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to mercury data results and proceed to next method in SDG.**	

2.0 Laboratory Method

2.1	Yes ___	No ___	N/A ___	Was the correct SW-846 method used for preparation and analysis of samples? [water: SW-846 7470A; soil: SW-846 7471A]	
2.2	Yes ___	No ___	N/A ___	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL. Results reported between the MDL and PQL are flagged J.	

Initial Review by: _____ Date: _____ SDG# _____
Senior Review by: _____ Date: _____ Matrix _____

3.0 Initial Calibration

					Notes
3.1	Yes	No	N/A	Were all instruments calibrated daily with a blank and 1 standard, or. with at least 3 standards and a blank? (r should be ≥ 0.995) If any instrument was not calibrated daily, reject (R) all associated data.	
3.2	Yes	No	N/A	Was a low level check standard analyzed after calibration at the method reporting level? Record SDG page number/s.	
3.3	Yes	No	N/A	Did the low-level check (LLC) standard recover within ±20% of the expected value? If not, flag associated non-detects J. Positive results do not require qualification for LLC std. performance.	
3.4	Yes	No	N/A	Are at least 3 exposures being averaged for mercury in soil?	
3.5	Yes	No	N/A	Was the alternate source midpoint calibration check standard within ± 10% of the true value? (ICV from section 4.0 may be used) If the alternate source midpoint calibration check standard recovery is outside the QC limits, flag results J.	

4.0 Continuing Calibration

4.1	Yes	No	N/A	Was an ICV analyzed immediately after calibration and within ± 10% of the true value? (The 2nd source standard mentioned in section 3.0 may be used.) Record SDG page numbers and any affected samples. If the ICV recovery is outside the QC limits, flag results J.	
4.2	Yes	No	N/A	Was a CCV analyzed every 10 samples and at the end of the sequence?	
4.3	Yes	No	N/A	Were the CCV's within ± 10% of the true value? Record SDG page numbers and any affected samples. If the CCV recovery is outside the QC limits, flag results J.	

5.0 Method Blanks

5.1	Yes	No	N/A	Was an Initial Calibration Blank (ICB) analyzed after the calibration?	

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					Notes
5.2	Yes	No	N/A	Does the ICB have positive results? If the sample concentration is ≤5x the blank value, assign a "B" If the sample concentration is >5x the blank value, no flag required.	
5.3	Yes	No	N/A	Was a Continuing Calibration Blank (CCB) analyzed every 10 samples and before each CCV to confirm sample path is clean of internal cross contamination? Record SDG page numbers.	
5.4	Yes	No	N/A	Do the subsequent CCB's have positive results? Note ID of blank and and affected samples. Samples are associated with samples run before and after the CCB. If the sample concentration is ≤5x the blank value, assign a "B" If the sample concentration is >5x the blank value, no flag required.	
5.5	Yes	No	N/A	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix? Record SDG page numbers.	
5.6	Yes	No	N/A	Does the Method Blank have positive results? If the sample concentration is ≤5x the blank value, assign a "B" If the sample concentration is >5x the blank value, no flag required.	

6.0 Laboratory Control Standard (LCS)

6.1	Yes	No	N/A	Is the LCS and/or LCS duplicate summary form present? Record SDG page number/s.	
6.2	Yes	No	N/A	Was an LCS analyzed with each SDG or every 20 samples of similar matrix?	
6.3	Yes	No	N/A	Are spiked recoveries within 80-120% in the LCS/LCSD? Flag results only if **both** the LCS and LCSD recoveries were outside the limits Flag Criteria: Hits in sample that fail high in the LCS = J Hits and NDs that fail low in the LCS = J	

7.0 Matrix Spikes

7.1	Yes	No	N/A	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Record SDG page number/s.	

					Notes
7.2	Yes	No	N/A	Were MS/MSDs analyzed at a frequency of 1 per 20 samples as designated by the project team? List samples that were spiked.	
7.3	Yes	No	N/A	Were the recoveries of the MS/MSD within COE Shell document limits (75%-125% recovery)? No calculation of recovery necessary if element is present in parent sample ≥ 4x the spike amount and no flags are applied. If recoveries are high, flag positive results in the parent sample "J". If recoveries are low, flag positive and non-detect results in the parent sample "J".	
7.4	Yes	No	N/A	Was the RPD between the MS/MSD < 25%? If not, flag results J.	

8.0 Duplicates

8.1	Yes	No	N/A	Were any intra-laboratory or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC Record and cross-reference sample ID along with SDG page number/s.	
8.2	Yes	No	N/A	Is RPD between sample and duplicate < 25%? If not, list sample ID, concentration of both samples and RPD. Record SDG page number/s. If RPD is greater than 25%, flag as estimated (J)	

9.0 Special QA/QC

9.1	Yes	No	N/A	Were both total and dissolved metals analysis performed? If so, the dissolved metal concentration should not exceed that of the total metal. If results for both total and dissolved are ≥ 5x the PQL **and** the dissolved concentration is 10% higher than the total, flag both results as estimated (J). If total and dissolved concentrations are less than 5x the PQL **and** the **difference** exceeds 2x the PQL, flag both results as estimated (J).	
9.2	Yes	No	N/A	Was a post digestion spike (PDS) performed in this SDG as needed to confirm matrix effect? If so, list sample affected. Record SDG page number/s.	

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					Notes
9.3	Yes	No	N/A	Was the recovery between 85-115% for mercury? List recoveries not meeting the criteria and flag per the following criteria: If PDS recovery is >115%, flag positive results "J" If PDS recovery is <85%, flag both positive and non-detect results "J".	
9.4	Yes	No	N/A	Was a Serial Dilution (SD) performed as needed to assess new and unusual matrices? If so, list sample affected. Agreement between undiluted and diluted results should be ≤ 10% for *mercury present at **50x** the DL*. If >10%, qualify results "J" Record SDG page number/s.	
9.5	Yes	No	N/A	If matrix effect is suspected or confirmed, was Method of Standard Addition (MSA) utilized to quantitate mercury? For detailed information on MSA, see project chemist.	
9.6	Yes	No	N/A	Was the correlation coefficient (r) of the MSA curve ≥ 0.995? If less than 0.995, qualify result as estimated (J).	
9.7	Yes	No	N/A	Is the slope of the MSA curve within ± 20% of the slope of the standard curve? If not, qualify the result as estimated (J).	

10.0 Compound Quantitation and Reported Detection Limits

10.1	Yes	No	N/A	Are results present for all samples sent to the lab for mercury? Compare COC with lab reports on a sample by sample basis.	
10.2	Yes	No	N/A	Have PQLs been adjusted to properly reflect sample dilutions and for soil, sample moisture and weight?	
10.3	Yes	No	N/A	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis	
10.4	Yes	No	N/A	Are all results within the linear range of calibration for each element requested?	

11.0 Field QA/QC

11.1	Yes	No	N/A	Were any rinsate blanks collected?	

					Notes
11.2	Yes	No	N/A	Is mercury detected in the rinsate blank? If so, list compounds present with concentration and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	
	___	___	___		

12.0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables, reviewer will initial and date tables. A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e g internal use only). This narrative will address all qualifiers associated with each method.

Data Usable With Qualification

J	Estimated quantitation based upon QC data
B	Estimated quantitation possibly biased high or false positive based upon blank data

Unusable Data

R	Data rejected based upon QC data

Flagging Hierarchy

R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Inorganic Data Review, 1999".
USACE "Shell for Analytical Chemistry Requirements", 1 February 2001.

8172277

Initial Review by: _____ Date: _____ SDG# _____
Senior Review by: _____ Date: _____ Matrix _____

SUPPLEMENTAL NOTES

Section Heading

8772278

DQE SW-846 6010B Rev. 05/14/04
(metals)

Initial Review by: _____ Date: _____ SDG# _____
Senior Review by: _____ Date: _____ Matrix _____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
SW-846 6010B
(Metals)

Note: The following Data Quality Evaluation (DQE) for SW-846 6010B (metals) as performed by Severn Trent Laboratories – North Canton, OH will be evaluated according to the QA/QC program outlined in the US Army Corp of Engineers Shell Document. In cases where data does not meet criteria, record the SDG page number for reference in lieu of copying. This checklist is not intended to be all encompassing and assumes personnel utilizing these forms are knowledgeable in data review. If at any time there is a questionable issue, consult the senior chemist.

1.0 Sample Integrity

					Notes
1.1	Yes ___	No ___	N/A ___	Were all samples sent to laboratory for dissolved metals analysis filtered before preservation? See the field Daily Quality Control Report (DQCR), field logs and/or sampling personnel for this information If extenuating circumstances did not allow for filtering, list samples affected.	
1.2	Yes ___	No ___	N/A ___	Was the 6 month holding time met for metals? Holding time is calculated as time elapsed from sampling to analysis. If not, flag results J.	
1.2.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of metals samples? [water: 1 liter plastic with HNO_3 to pH<2 @ 4° C; soil: 8 oz. soil jar]	
1.2.2	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to metals data results and proceed to next method in SDG.**	

2.0 Laboratory Method

2.1	Yes ___	No ___	N/A ___	Was the correct SW-846 method used for preparation and analysis of samples? [water: SW-846 3005A/6010B; soil: SW-846 3050A/6010B]	
2.2	Yes ___	No ___	N/A ___	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL. Results reported between the MDL and PQL are flagged J.	

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Initial Review by: _____ Date: _____ SDG# _____
Senior Review by: _____ Date: _____ Matrix _____

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3.0 Initial Calibration

					Notes
3.1	Yes ___	No ___	N/A ___	Were all instruments calibrated daily with a blank and 1 standard, or. with at least 3 standards and a blank? (r should be ≥ 0.995) If any instrument was not calibrated daily, reject (R) all associated data.	
3.2	Yes ___	No ___	N/A ___	Was a low level check standard analyzed after calibration at the method reporting level? Record SDG page number/s.	
3.3	Yes ___	No ___	N/A ___	Did the low-level check (LLC) standard recover within ±20% of the expected value? If not, flag associated non-detects J. Positive results do not require qualification for LLC std. performance.	
3.4	Yes ___	No ___	N/A ___	Are at least 3 exposures being averaged for each element analyzed? Checking the raw data will reveal % RSD for the 3 exposures. RSD should be less than 5%. **Note:** Currently, STL – N. Canton averages 2 exposures as approved by the USACE.	
3.5	Yes ___	No ___	N/A ___	Was the alternate source midpoint calibration check standard within ± 10% of the true value? (ICV from section 4.0 may be used) If the alternate source midpoint calibration check standard recovery is outside the QC limits, flag results J.	
3.6	Yes ___	No ___	N/A ___	Were the Interference Check Samples analyzed before the analysis of samples? (ICS-A interferents only, ICS-B interferents and target analytes). Record SDG page number/s	
3.7	Yes ___	No ___	N/A ___	Were non-spiked analytes present > 2 times the PQL in ICS-A? If not, apply (J) flags to the element present in all samples associated with the ICS-A.	
3.8	Yes ___	No ___	N/A ___	Were target analytes recovered ± 20% of the true value? If any interference check standard exceeded criteria for an element, reject (R) all samples which were analyzed before this standard and all samples following the standard until an acceptable interference check standard was analyzed. Do not apply limits to the recovery of Al, Ca, Fe, Mg, and K	

					Notes
3.9	Yes	No	N/A	Has the instruments linear range been established with the analysis of a high standard containing each element? **Note:** Some laboratories may analyze this standard on a scheduled basis (e.g. monthly, quarterly, etc.). Each SDG should have a summary page indicating the recovery and when this standard was analyzed. List dates in the space provided.	

4.0 Continuing Calibration

4.1	Yes	No	N/A	Was an ICV analyzed immediately after calibration and within ± 10% of the true value? (The 2nd source standard mentioned in section 3.0 may be used.) Record SDG page numbers and any affected samples. If the ICV recovery is outside the QC limits, flag results J.	
4.2	Yes	No	N/A	Was a CCV analyzed every 10 samples and at the end of the sequence?	
4.3	Yes	No	N/A	Were the CCV's within ± 10% of the true value? Record SDG page numbers and any affected samples If the CCV recovery is outside the QC limits, flag results J	

5.0 Method Blanks

5.1	Yes	No	N/A	Was an Initial Calibration Blank (ICB) analyzed after the calibration?	
5.2	Yes	No	N/A	Does the ICB have positive results? If the sample concentration is ≤5x the blank value, assign a "B" If the sample concentration is >5x the blank value, no flag required.	
5.3	Yes	No	N/A	Was a Continuing Calibration Blank (CCB) analyzed every 10 samples and before each CCV to confirm sample path is clean of internal cross contamination? Record SDG page numbers.	
5.4	Yes	No	N/A	Do the subsequent CCB's have positive results? Note ID of blank and and affected samples. Samples are associated with samples run before and after the CCB. If the sample concentration is ≤5x the blank value, assign a "B" If the sample concentration is >5x the blank value, no flag required.	

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					Notes
5.5	Yes ___	No ___	N/A ___	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix? Record SDG page numbers.	
5.6	Yes ___	No ___	N/A ___	Does the Method Blank have positive results? If the sample concentration is ≤5x the blank value, assign a "B" If the sample concentration is >5x the blank value, no flag required.	

6.0 Laboratory Control Standard (LCS)

6.1	Yes ___	No ___	N/A ___	Is the LCS and/or LCS duplicate summary form present? Record SDG page number/s.	
6.2	Yes ___	No ___	N/A ___	Was an LCS analyzed with each SDG or every 20 samples of similar matrix?	
6.3	Yes ___	No ___	N/A ___	Are spiked recoveries within 80-120% in the LCS/LCSD? The COE Shell document allows for sporadic marginal failures Expanded limits are 60-140% recovery. If between 7 to 15 metals are reported: one failure allowed. If greater than 15 metals reported: two failures allowed Flag results only if **both** the LCS and LCSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the LCS = J Hits and NDs that fail low in the LCS = J	

7.0 Matrix Spikes

7.1	Yes ___	No ___	N/A ___	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Record SDG page number/s.	
7.2	Yes ___	No ___	N/A ___	Were MS/MSDs analyzed at a frequency of 1 per 20 samples as designated by the project team? List samples that were spiked.	
7.3	Yes ___	No ___	N/A ___	Were the recoveries of the MS/MSD within COE Shell document limits (75%-125% recovery)? No calculation of recovery necessary if element is present in parent sample ≥ 4x the spike amount and no flags are applied. If recoveries are high, flag positive results in the parent sample "J". If recoveries are low, flag positive and non-detect results in the parent sample "J"	

					Notes
7.4	Yes	No	N/A	Was the RPD between the MS/MSD < 25%? If not, flag results J.	
	—	—	—		

8.0 Duplicates

8.1	Yes	No	N/A	Were any intra-laboratory or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC. Record and cross-reference sample ID along with SDG page number/s.	
	—	—	—		
8.2	Yes	No	N/A	Is RPD between sample and duplicate < 25%? If not, list sample ID, concentration of both samples and RPD. Record SDG page number/s. If RPD is greater than 25%, flag as estimated (J).	
	—	—	—		

9.0 Special QA/QC

9.1	Yes	No	N/A	Were both total and dissolved metals analysis performed? If so, the dissolved metal concentration should not exceed that of the total metal. If results for both total and dissolved are ≥ 5x the PQL **and** the dissolved concentration is 10% higher than the total, flag both results as estimated (J). If total and dissolved concentrations are less than 5x the PQL **and** the **difference** exceeds 2x the PQL, flag both results as estimated (J).	
	—	—	—		
9.2	Yes	No	N/A	Was a post digestion spike (PDS) performed in this SDG as needed to confirm matrix effect? If so, list sample affected. Record SDG page number/s.	
	—	—	—		
9.3	Yes	No	N/A	Was the recovery between 85-115% for all or a subset of target analytes? List recoveries of those elements not meeting the criteria and flag per the following criteria: If PDS recovery is >115%, flag positive results "J". If PDS recovery is <85%, flag both positive and non-detect results "J".	
	—	—	—		
9.4	Yes	No	N/A	Was a Serial Dilution (SD) performed as needed to assess new and unusual matrices? If so, list sample affected. Agreement between undiluted and diluted results should be ≤ 10% for *any metal present at **50x** the DL*. If >10%, qualify results "J". Record SDG page number/s.	
	—	—	—		

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					Notes
9.5	Yes	No	N/A	If matrix effect is suspected or confirmed, was Method of Standard Addition (MSA) utilized to quantitate any of the metals? For detailed information on MSA, see project chemist.	
9.6	Yes	No	N/A	Was the correlation coefficient (r) of the MSA curve ≥ 0.995? If less than 0.995, qualify result as estimated (J).	
9.7	Yes	No	N/A	Is the slope of the MSA curve within ± 20% of the slope of the standard curve? If not, qualify the result as estimated (J).	

10.0 Compound Quantitation and Reported Detection Limits

10.1	Yes	No	N/A	Are results present for all samples sent to the lab for metals? Compare COC with lab reports on a sample by sample basis	
10.2	Yes	No	N/A	Have PQLs been adjusted to properly reflect sample dilutions and for soil, sample moisture and weight?	
10.3	Yes	No	N/A	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis.	
10.4	Yes	No	N/A	Are all results within the linear range of calibration for each element requested?	

11.0 Field QA/QC

11.1	Yes	No	N/A	Were any rinsate blanks collected?	
11.2	Yes	No	N/A	Are target analytes less than PQLs in the rinsate blank? If not, list compounds present with concentration and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary.	

12.0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables, reviewer will initial and date tables. A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e g. internal use only). This narrative will address all qualifiers associated with each method.

	Data Usable With Qualification
J	Estimated quantitation based upon QC data
B	Estimated quantitation: possibly biased high or false positive based upon blank data
	Unusable Data
R	Data rejected based upon QC data
	Flagging Hierarchy
	R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Inorganic Data Review, 1999".
USACE "Shell for Analytical Chemistry Requirements", 1 February 2001.

8772285

Initial Review by: _____ Date: _____ SDG# _____
Senior Review by: _____ Date: _____ Matrix _____

SUPPLEMENTAL NOTES

Section Heading

8772286

DQE RSK-175 05/14/04
(methane, ethane, ethene, carbon dioxide)

Initial Review by:_____ Date:_____
Senior Review by:_____ Date:_____

SDG#_____
Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
RSK - 175
(Dissolved Gases)

Note: The following Data Quality Evaluation (DQE) for RSK - 175 (Dissolved Gases) as performed by STL - Los Angeles will be evaluated according to the labs QA/QC program. The COE Shell Document does not specifically address dissolved gases techniques. The laboratories QA/QC program in regards to this method should be modeled after standard SW-846 practices concerning hold times, calibration criteria, sequence QC (e.g. method blanks, LCS, MS/MSD, etc.) and detection limit determination. Specifically, Method 8000 will be used as a general guidance for this GC method under the auspices of a modified 8015 Method.

1.0 Sample Integrity

					Notes
1.1	Yes ___	No ___	N/A ___	Was the project specific 14 day holding time met for methane, ethane, and ethene? Was the project specific 7 day holding time met for carbon dioxide? Holding time is calculated as time elapsed from sampling to analysis. If not, flag sample results as J.	
1.1.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of the dissolved gases samples? [40 ml VOA vial with **HCl to pH <2 @ 4°C** for methane, ethane, and ethene and 40 ml VOA vial with **no preservative @ 4°C** for carbon dioxide]	
1.1.2	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to dissolved gases data results and proceed to next method in SDG.**	

2.0 Laboratory Method

2.1	Yes ___	No ___	N/A ___	Was the correct method used for analysis of dissolved gases? [RSK - 175 respectively]	
2.2	Yes ___	No ___	N/A ___	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL Results reported between the MDL and PQL are flagged J.	

3.0 Initial Calibration

3.1	Yes ___	No ___	N/A ___	Are the Initial Calibration forms present with at least 5 calibration levels for each gas? Record SDG page number/s.	

Initial Review by:_____Date:_____ SDG#_____
Senior Review by:_____Date:_____ Matrix_____

					Notes
3.2	Yes ___	No ___	N/A ___	Is the initial calibration correlation coefficient (r) ≥ 0.995 or (r^2) ≥ 0.990 or %RSD ≤ 25%? If not, flag sample results R (rejected)	
3.3	Yes ___	No ___	N/A ___	If %RSD is greater than 25%, is the average of all compound Response Factors (RFs) less than 25% RSD? If not, flag sample results R (rejected).	

4.0 Continuing Calibration

4.1	Yes ___	No ___	N/A ___	Are CCV recovery forms present? Record SDG page number/s.	
4.2	Yes ___	No ___	N/A ___	Was a CCV analyzed at least every 24 hrs?	
4.3	Yes ___	No ___	N/A ___	Were the CCV's within ± 25%D/25% Drift of the true value? If not, note CCV number and samples affected in this SDG, if any. Flag sample results as J.	

5.0 Method Blanks

5.1	Yes ___	No ___	N/A ___	Is the Method Blank summary present? Record SDG page number/s.	
5.2	Yes ___	No ___	N/A ___	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix?	
5.3	Yes ___	No ___	N/A ___	Are all Method/Instrument/Reagent blanks less than the PQL? If not, did the lab take corrective action? List analytes present and concentration and apply the following: If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	

6.0 Laboratory Control Standard (LCS)

6.1	Yes ___	No ___	N/A ___	Was the LCS and/or LCS duplicate summary form present? Record SDG page number/s	

8772288

					Notes
6.2	Yes ___	No ___	N/A ___	Was an LCS analyzed with each SDG or every 20 samples of similar matrix?	
6.3	Yes ___	No ___	N/A ___	Are spiked recoveries within laboratory limits in the LCS/LCSD? Flag results only if **both** the LCS and LCSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the LCS = J Hits and NDs that fail low in the LCS = J	

7.0 Matrix Spikes – Matrix spike/matrix spike duplicate samples are not performed for dissolved gases analysis.

8.0 Duplicates

8.1	Yes ___	No ___	N/A ___	Were any intra-laboratory or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC Record and cross-reference sample ID along with SDG page number/s.	
8.2	Yes ___	No ___	N/A ___	Is RPD between sample and duplicate < 20%? If not, list sample ID, concentration of both samples and RPD. Per USEPA National Functional Guidelines, "No action is taken based on percent difference of field duplicate sample data alone However, using informed professional judgement, the data reviewer may use the field duplicate results in conjunction with other QC criteria to determine the need for some qualification of the data." Flag results J.	

9.0 Compound Quantitation and Reported Detection Limits

9.1	Yes ___	No ___	N/A ___	Are results present for all samples sent to the lab for dissolved gases?	
9.2	Yes ___	No ___	N/A ___	Have PQLs been adjusted to properly reflect sample dilutions?	
9.3	Yes ___	No ___	N/A ___	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis in the "Miscellaneous Data" section of RSK-175.	

8772289

Initial Review by:_____ Date:_____ SDG#_____
Senior Review by:_____ Date:_____ Matrix_____

10.0 Field QA/QC

					Notes
10.1	Yes	No	N/A	Were any rinsate blanks collected?	
10.2	Yes	No	N/A	Are target analytes present in the rinsate blank? List compounds present with concentration and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	
10.3	Yes	No	N/A	Were trip blanks shipped in the cooler with the field samples?	
10.4	Yes	No	N/A	Are target analytes present in the trip blank? List compounds present with concentration and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary Note: According to STL-Los Angeles SOP, CO2 and methane are common lab contaminants. Therefore, expect to see CO2 in any blank exposed to ambient air (e.g. ambient blanks and rinsate blanks). Consult Senior Chemist for further guidance in applying flags due to positive results in any field blank.	

8772290

11.0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables, reviewer will initial and date tables. A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e g. internal use only). This narrative will address all qualifiers associated with each method.

	Data Usable With Qualification
J	Estimated quantitation based upon QC data
B	Estimated quantitation possibly biased high or false positive based upon blank data
	Unusable Data
R	Data rejected based upon QC data
	Flagging Hierarchy
	R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Organic Data Review, 1994".

Severn Trent Laboratories - Los Angeles, "Sample Preparation and the Determination of Dissolved Gases in Water by Using GC Headspace Equilibrium Technique (EPA RSK SOP - 175) Modified", SOP No. COL-GC-005, Rev. 0 (04/24/1998).

USEPA SW-846 Update III

Initial Review by:_____Date:_____
Senior Review by:_____Date:_____

SDG#_____
Matrix_____

SUPPLEMENTAL NOTES

Section Heading

8772292

DQE SW-846 9060 Rev. 05/14/04
(Total and Dissolved Organic Carbon)

Initial Review by:_____ Date:_____
Senior Review by:_____ Date:_____

SDG#_____
Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
SW-846 9060/Walkley-Black
(Total and Dissolved Organic Carbon)

Note: The following Data Quality Evaluation (DQE) for SW-846 9060 (TOC and DOC) and Walkley-Black (TOC) as performed by Severn Trent Laboratory – North Canton will be evaluated according to the labs QA/QC program. The COE Shell Document does not specifically address wet chemistry techniques.

					Notes
1.0 Sample Integrity					
1.1	Yes ___	No ___	N/A ___	Was the 28 day holding time met for TOC/DOC analysis? Holding time is calculated as time elapsed from sampling to analysis If not, flag results J.	
1.1.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of TOC/DOC samples? [Water: 3x40ml VOA vials with H_2SO_4 to pH < 2 @ 4° C; DOC field filtered before preservation Soil (TOC): 1x8oz. glass jar @ 4° C]	
1.1 2	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to TOC/DOC data results and proceed to next method in SDG.**	
2.0 Laboratory Method					
2 1	Yes ___	No ___	N/A ___	Was the correct method used for analysis of TOC/DOC? [Water: SW-846 9060, Soil: Walkley Black]	
2.2	Yes ___	No ___	N/A ___	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL Results reported between the MDL and PQL are flagged J.	
3.0 Initial Calibration					
3.1	Yes ___	No ___	N/A ___	Are the Initial Calibration forms present with at least 3 calibration levels for TOC/DOC? Record SDG page numbers.	

Initial Review by:_____ Date:_____ SDG#_____
Senior Review by:_____ Date:_____ Matrix_____

8772294

					Notes
3.2	Yes	No	N/A	Is the initial calibration linear, with a correlation coefficient (r) ≥ 0.995? **or** if Average Response Factor (RF) was used, is the RSD ≤ 20%? If not, flag results J.	
3.3	Yes	No	N/A	Was an Initial Calibration Verification (ICV) standard analyzed at the beginning of a daily sequence and within ± 10% of the true value? Record SDG page numbers. If not, flag results J.	

4.0 Continuing Calibration

4.1	Yes	No	N/A	Was a CCV analyzed every 10 samples and at the end of the sequence? Record SDG page numbers.	
4.2	Yes	No	N/A	Were the CCV's within ± 10% of the true value? If not, note CCV number and samples affected. If not, flag results J.	

5.0 Method Blanks

5.1	Yes	No	N/A	Is the Method Blank summary present? Record SDG page numbers.	
5.2	Yes	No	N/A	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix?	
5.3	Yes	No	N/A	Was a blank analyzed every 10 samples, before or after a CCV to confirm sample path is clean of internal cross contamination?	
5.4	Yes	No	N/A	Are all Method/Instrument/Reagent blanks less than the PQL? If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary.	

6.0 Laboratory Control Standard (LCS)

6.1	Yes	No	N/A	Is the LCS and/or LCS duplicate summary form present? Record SDG page numbers.	
6.2	Yes	No	N/A	Was an LCS analyzed with each SDG or every 20 samples of similar matrix?	

					Notes
6.3	Yes ___	No ___	N/A ___	Are spiked recoveries within laboratory limits in the LCS/LCSD? Flag results only if **both** the LCS and LCSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the LCS = J Hits and NDs that fail low in the LCS = J	

7.0 Matrix Spikes

7.1	Yes ___	No ___	N/A ___	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Record SDG page numbers	
7.2	Yes ___	No ___	N/A ___	Were MS/MSDs analyzed at a frequency of 1 per 20 samples as designated by project team? List samples that were spiked.	
7.3	Yes ___	No ___	N/A ___	Were the recoveries of the MS/MSD within laboratory limits? Flag results only if **both** the MS and MSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the MS/MSD = J Hits and NDs that fail low in the MS/MSD = J	
7.4	Yes ___	No ___	N/A ___	Was the RPD between the MS/MSD < 20%? If not, flag results J.	

8.0 Duplicates

8.1	Yes ___	No ___	N/A ___	Were any intra-laboratory or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC. Record and cross-reference sample ID along with SDG page numbers.	
8.2	Yes ___	No ___	N/A ___	Is RPD between sample and duplicate < 20%? If not, list sample ID, concentration of both samples and RPD. Per USEPA National Functional Guidelines, "No action is taken based on percent difference of field duplicate sample data alone. However, using informed professional judgement, the data reviewer may use the field duplicate results in conjunction with other QC criteria to determine the need for some qualification of the data." Flag results J.	

Initial Review by:_____ Date:_____
Senior Review by:_____ Date:_____

SDG#_____
Matrix_____

9.0 Compound Quantitation and Reported Detection Limits

					Notes
9.1	Yes	No	N/A	Are results present for all samples sent to the lab for TOC/DOC?	
	___	___	___		
9.2	Yes	No	N/A	Have PQLs been adjusted to properly reflect sample dilutions?	
	___	___	___		
9.3	Yes	No	N/A	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis.	
	___	___	___		

10.0 Field QA/QC

10.1	Yes	No	N/A	Were any rinsate blanks collected? Record SDG page numbers.	
	___	___	___		
10.2	Yes	No	N/A	Is TOC/DOC less than PQLs in the rinsate blank? If not, list compounds present with concentration and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B" If sample concentration is > 5x the blank value, no flag is necessary	
	___	___	___		

8772296

11.0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables, reviewer will initial and date tables. A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e.g. internal use only). This narrative will address all qualifiers associated with each method.

	Data Usable With Qualification
J	Estimated quantitation based upon QC data
B	Estimated quantitation: possibly biased high or false positive based upon blank data
	Unusable Data
R	Data rejected based upon QC data
	Flagging Hierarchy
	R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Inorganic Data Review, 1999".

Initial Review by:_____Date:_____ SDG#_____
Senior Review by:_____Date:_____ Matrix_____

SUPPLEMENTAL NOTES

Section Heading

8772298

DQE MCAWW 300.0 Rev. 05/14/04
(bromide, chloride, nitrate, nitrite, and sulfate)

Initial Review by:_____ Date._____
Senior Review by:_____ Date:_____

SDG#_____
Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
MCAWW 300.0
(Anions)

Note: The following Data Quality Evaluation (DQE) for MCAWW 300.0 (anions) as performed by Severn Trent Laboratory – North Canton will be evaluated according to the labs QA/QC program. The COE Shell Document does not specifically address ion chromatography techniques.

					Notes
1.0 Sample Integrity					
1.1	Yes ___	No ___	N/A ___	Was the project specific 48 hour holding time met for nitrate and nitrite? Holding time is calculated as time elapsed from sampling to analysis. Note: Standard holding time for bromide, chloride, and sulfate is 28 days. If not, flag sample results as J.	
1.1.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of anions sample? [250 ml plastic with no preservative @ 4° C]	
1.1.2	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to anions data results and proceed to next method in SDG.**	
2.0 Laboratory Method					
2.1	Yes ___	No ___	N/A ___	Was the correct method used for analysis of anions? [MCAWW 300.0]	
2.2	Yes ___	No ___	N/A ___	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL. Results reported between the MDL and PQL are flagged "J"	
3.0 Initial Calibration					
3.1	Yes ___	No ___	N/A ___	Are the Initial Calibration forms present with at least 5 calibration levels for anions? Record SDG page number/s.	
3.2	Yes ___	No ___	N/A ___	If quadratic curve was used, have at least 6 standards been analyzed and included in the calibration? Excluding the origin. Note: STL currently uses 5 standards. (No flags applied at this time)	

8772299

					Notes
3.3	Yes	No	N/A	Is the initial calibration correlation coefficient (r) ≥ 0.995? **or** if Average Response Factor (RF) was used, is the RSD ≤ 20%? If not, flag sample results R (rejected).	
3.4	Yes	No	N/A	Was an alternate source midpoint calibration check standard analyzed before the analysis of samples?	
3.5	Yes	No	N/A	Was the midpoint calibration check standard within ± 10% of the true value? If not, flag sample results as J.	

4.0 Continuing Calibration

4.1	Yes	No	N/A	Are ICV/CCV recovery forms present? Record SDG page number/s	
4.2	Yes	No	N/A	Was an ICV analyzed immediately after calibration and within ± 10% of the true value? If not, flag results J.	
4.3	Yes	No	N/A	Was a CCV analyzed every 10 samples and at the end of the sequence?	
4.4	Yes	No	N/A	Were the CCV's within ± 10% of the true value? If not, note CCV number and samples affected in this SDG, if any. Flag sample results as J.	

5.0 Method Blanks

5.1	Yes	No	N/A	Is the Method Blank summary present? Record SDG page number/s.	
5.2	Yes	No	N/A	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix?	
5.3	Yes	No	N/A	Was a blank analyzed every 10 samples, before a CCV and after a CCV to confirm sample path is clean of internal cross contamination?	

8772300

					Notes
5.4	Yes	No	N/A	Are all Method/Instrument/Reagent blanks less than the PQL? If not, did the lab take corrective action? List analytes present and concentration and apply the following: If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	

6.0 Laboratory Control Standard (LCS)

6.1	Yes	No	N/A	Is the LCS and/or LCS duplicate summary form present? Record SDG page number/s.	
6.2	Yes	No	N/A	Was an LCS analyzed with each SDG or every 20 samples of similar matrix?	
6.3	Yes	No	N/A	Are spiked recoveries within laboratory limits in the LCS/LCSD? Flag results only if **both** the LCS and LCSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the LCS = J Hits and NDs that fail low in the LCS = J	

7.0 Matrix Spikes

7.1	Yes	No	N/A	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Record SDG page number/s.	
7.2	Yes	No	N/A	Were MS/MSDs analyzed at a frequency of 1 per 20 samples and if designated by project team, were proper samples spiked? If not, list samples that were spiked	
7.3	Yes	No	N/A	Were the recoveries of the MS/MSD within laboratory limits? Flag results only if **both** the MS and MSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the MS/MSD = J Hits and NDs that fail low in the MS/MSD = J	
7.4	Yes	No	N/A	Was the RPD between the MS/MSD < 20%? If not, flag results J.	

8772301

8.0 Duplicates

					Notes
8.1	Yes ___	No ___	N/A ___	Were any intra-laboratory or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC. Record and cross-reference sample ID along with SDG page number/s	
8.2	Yes ___	No ___	N/A ___	Is RPD between sample and duplicate < 20%? If not, list sample ID, concentration of both samples and RPD. Per USEPA National Functional Guidelines, "No action is taken based on percent difference of field duplicate sample data alone. However, using informed professional judgement, the data reviewer may use the field duplicate results in conjunction with other QC criteria to determine the need for some qualification of the data." Flag results J	

9.0 Compound Quantitation and Reported Detection Limits

9.1	Yes ___	No ___	N/A ___	Are results present for all samples sent to the lab for anions?	
9.2	Yes ___	No ___	N/A ___	Have PQLs been adjusted to properly reflect sample dilutions?	
9.3	Yes ___	No ___	N/A ___	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis.	

10.0 Field QA/QC

10.1	Yes ___	No ___	N/A ___	Were any rinsate blanks collected?	
10.2	Yes ___	No ___	N/A ___	Are target analytes present in the rinsate blank? List compounds present with concentration and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B" If sample concentration is > 5x the blank value, no flag is necessary	

8772302

11.0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables, reviewer will initial and date tables. A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e.g. internal use only). This narrative will address all qualifiers associated with each method.

	Data Usable With Qualification
J	Estimated quantitation based upon QC data
B	Estimated quantitation: possibly biased high or false positive based upon blank data
	Unusable Data
R	Data rejected based upon QC data
	Flagging Hierarchy
	R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Inorganic Data Review, 1999".

Initial Review by:_____Date:_____
Senior Review by _____Date:_____

SDG#_____
Matrix_____

SUPPLEMENTAL NOTES

Section Heading

8772304

DQE MCAWW 310.1 Rev. 05/14/04
(Alkalinity)

Initial Review by:_____ Date:_____
Senior Review by:_____ Date:_____

SDG#_____
Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
MCAWW 310.1
(Alkalinity)

Note: The following Data Quality Evaluation (DQE) for MCAWW 310.1 (alkalinity) as performed by Severn Trent Laboratory – North Canton will be evaluated according to the labs QA/QC program. The COE Shell Document does not specifically address wet chemistry techniques.

1.0 Sample Integrity

					Notes
1.1	Yes ___	No ___	N/A ___	Was the project specific 14 day holding time met for alkalinity? Holding time is calculated as time elapsed from sampling to analysis. If not, flag results J.	
1.1.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of alkalinity samples? [500 mL plastic with no preservative @ 4° C]	
1.1.2	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to alkalinity data results and proceed to next method in SDG.**	

2.0 Laboratory Method

2.1	Yes ___	No ___	N/A ___	Was the correct method used for analysis of alkalinity? [MCAWW 310.1]	
2.2	Yes ___	No ___	N/A ___	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL. Results reported between the MDL and PQL are flagged J.	

3.0 Initial Calibration

3.1	Yes ___	No ___	N/A ___	Was the pH meter calibrated daily with at least two calibration standards (typically pH 4 and pH 7)? Record SDG page numbers.	
3.2	Yes ___	No ___	N/A ___	Is the initial calibration correlation coefficient (r) ≥ 0.995? Note: This only applies if more than two standards were analyzed. If only two standards were analyzed, then correlation will always be 1.0. If not, flag associated sample results R (rejected).	

8772305

					Notes
3.3	Yes	No	N/A	Was a calibration check standard analyzed at pH 10 before the analysis of samples? Record SDG page numbers.	
3.4	Yes	No	N/A	Was the calibration check standard at pH 10 within ± 10% of the true value? If not, flag results J	

4.0 Continuing Calibration

4.1	Yes	No	N/A	Was an ICV analyzed immediately after calibration and within ± 10% of the true value? If not, flag results J. The calibration check from section 3.3 above may be used.	
4.2	Yes	No	N/A	Was a CCV analyzed every 10 samples and at the end of the sequence?	
4.3	Yes	No	N/A	Were the CCV's within ± 10% of the true value? If not, flag results J	
4.4	Yes	No	N/A	Was the titrant standardized? Note standardization date, standardization expiration date, and SDG page numbers.	
4.4.1	Yes	No	N/A	Were any samples in this SDG analyzed after the expiration of the titrant? If so, apply "R" flag to all associated samples.	

5 0 Method Blanks

5.1	Yes	No	N/A	Is the Method Blank summary present? Record SDG page numbers.	
5.2	Yes	No	N/A	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix?	
5.3	Yes	No	N/A	Are all Method Blanks less than the PQL? If not, the lab should have performed corrective action. List the method blanks and alkalinity values and apply the following: If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	

8772306

6.0 Laboratory Control Standard (LCS)

					Notes
6.1	Yes ___	No ___	N/A ___	Is the LCS and/or LCS duplicate summary form present? Record SDG page number/s.	
6.2	Yes ___	No ___	N/A ___	Was an LCS analyzed with each SDG or every 20 samples of similar matrix?	
6.3	Yes ___	No ___	N/A ___	Are spiked recoveries within laboratory limits in the LCS/LCSD? Flag results only if **both** the LCS and LCSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the LCS = J Hits and NDs that fail low in the LCS = J	

7.0 Matrix Spikes

7.1	Yes ___	No ___	N/A ___	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Record SDG page number/s.	
7.2	Yes ___	No ___	N/A ___	Were MS/MSDs analyzed at a frequency of 1 per 20 samples as designated by project team? List sample that was spiked.	
7.3	Yes ___	No ___	N/A ___	Were the recoveries of the MS/MSD within laboratory limits? Flag results only if **both** the MS and MSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the MS/MSD = J Hits and NDs that fail low in the MS/MSD = J	
7.4	Yes ___	No ___	N/A ___	Was the RPD between the MS/MSD < 20%? If not, flag results J	

8.0 Duplicates

8.1	Yes ___	No ___	N/A ___	Were any intra-laboratory or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC. Record and cross-reference sample ID along with SDG page number/s.	

8772308

					Notes
8.2	Yes ___	No ___	N/A ___	Is RPD between sample and duplicate < 20%? If not, list sample ID, concentration of both samples and RPD. Per USEPA National Functional Guidelines, "No action is taken based on percent difference of field duplicate sample data alone However, using informed professional judgement, the data reviewer may use the field duplicate results in conjunction with other QC criteria to determine the need for some qualification of the data " Flag results J	

9.0 Compound Quantitation and Reported Detection Limits

9.1	Yes ___	No ___	N/A ___	Are results present for all samples sent to the lab for alkalinity?	
9.2	Yes ___	No ___	N/A ___	Have PQLs been adjusted to properly reflect sample dilutions?	
9.3	Yes ___	No ___	N/A ___	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis.	

10 0 Field QA/QC

10.1	Yes ___	No ___	N/A ___	Were any rinsate blanks collected?	
10.2	Yes ___	No ___	N/A ___	Are target analytes present in the rinsate blank? List compounds present with concentration and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary.	

11.0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables, reviewer will initial and date tables. A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e g. internal use only). This narrative will address all qualifiers associated with each method.

	Data Usable With Qualification
J	Estimated quantitation based upon QC data
B	Estimated quantitation. possibly biased high or false positive based upon blank data
	Unusable Data
R	Data rejected based upon QC data
	Flagging Hierarchy
	R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Inorganic Data Review, 1999".

Initial Review by:_____Date:_____
Senior Review by _____Date_____

SDG#_____
Matrix_____

SUPPLEMENTAL NOTES

Section Heading

8772310

Initial Review by:_____ Date:_____ SDG#_____
Senior Review by:_____ Date:_____ Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
MCAWW 376.1
(Sulfide)

Note: The following Data Quality Evaluation (DQE) for MCAWW 376.1 (sulfide) as performed by Severn Trent Laboratory – North Canton will be evaluated according to the labs QA/QC program. The COE Shell Document does not specifically address wet chemistry techniques.

1.0 Sample Integrity

					Notes
1.4	Yes ___	No ___	N/A ___	Was the project specific 7 day holding time met for sulfide? Holding time is calculated as time elapsed from sampling to analysis. If not, flag results J.	
1.4.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of sulfide samples? [500 ml plastic with **NaOH and zinc acetate** @ 4° C]	
1.4.2	Yes ___	No ___	N/A ___	**Should DQE proceed? If No, apply "R" to sulfide data results and proceed to next method in SDG.**	

2.0 Laboratory Method

2.1	Yes ___	No ___	N/A ___	Was the correct method used for analysis of sulfide? [MCAWW 376.1]	
2.2	Yes ___	No ___	N/A ___	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL. Results reported between the MDL and PQL are flagged J	

3.0 Initial Calibration

This method is titrametric and does not require a multiple level calibration. However, the laboratory should be using standardized solutions and the dates of standardization should be noted. See Section 4.0 for notation of solution standardization.

4.0 Continuing Calibration

4.1	Yes ___	No ___	N/A ___	Was an ICV analyzed immediately after calibration and within ± 10% of the true value? If not, flag results J	

Initial Review by:_____ Date:_____ SDG#_____
Senior Review by:_____ Date:_____ Matrix_____

					Notes
4.2	Yes	No	N/A	Was a CCV analyzed every 10 samples and at the end of the sequence?	
	___	___	___		
4 3	Yes	No	N/A	Were the CCV's within ± 10% of the true value? If not, flag results J.	
	___	___	___		
4.4	Yes	No	N/A	Was the titrant standardized? Date:_____ If not, when does standardization expire? Date:_____ Note SDG page number/s.	
	___	___	___		
4.4.1	Yes	No	N/A	Were any samples in this SDG analyzed after the expiration of the titrant? If so, apply "R" flag to all associated samples.	
	___	___	___		

5.0 Method Blanks

5.1	Yes	No	N/A	Is the Method Blank summary present? Note SDG page number/s.	
	___	___	___		
5.2	Yes	No	N/A	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix?	
	___	___	___		
5.3	Yes	No	N/A	Are all Method/Instrument/Reagent blanks less than the PQL? If not, lab should perform corrective action. List analyte and concentration present and apply the following : If sample concentration is ≤ 5x the blank value, assign a "B" If sample concentration is > 5x the blank value, no flag is necessary	
	___	___	___		

6.0 Laboratory Control Standard (LCS)

6 1	Yes	No	N/A	Is the LCS and/or LCS duplicate summary form present? Note SDG page number/s.	
	___	___	___		
6.2	Yes	No	N/A	Was an LCS analyzed with each SDG or every 20 samples of similar matrix?	
	___	___	___		

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					Notes
6 3	Yes	No	N/A	Are spiked recoveries within laboratory limits in the LCS/LCSD? Flag results only if **both** the LCS and LCSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the LCS = J Hits and NDs that fail low in the LCS = J	

7.0 Matrix Spikes

7.1	Yes	No	N/A	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Note SDG page number/s.	
7.2	Yes	No	N/A	Were MS/MSDs analyzed at a frequency of 1 per 20 samples and if designated by project team, were proper samples spiked? If not list sample that was spiked.	
7.3	Yes	No	N/A	Were the recoveries of the MS/MSD within laboratory limits? Flag results only if **both** the MS and MSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the MS/MSD = J Hits and NDs that fail low in the MS/MSD = J	
7.4	Yes	No	N/A	Was the RPD between the MS/MSD < 20%? If not, flag results J.	

8.0 Duplicates

8.1	Yes	No	N/A	Were any intra-laboratory or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC. Record and cross-reference sample ID along with SDG page number/s.	

					Notes
8.2	Yes	No	N/A	Is RPD between sample and duplicate < 20%? If not, list sample ID, concentration of both samples and RPD. Per USEPA National Functional Guidelines, "No action is taken based on percent difference of field duplicate sample data alone However, using informed professional judgement, the data reviewer may use the field duplicate results in conjunction with other QC criteria to determine the need for some qualification of the data." Flag results J.	

9.0 Compound Quantitation and Reported Detection Limits

9.1	Yes	No	N/A	Are results present for all samples sent to the lab for sulfide?	
9.2	Yes	No	N/A	Have PQLs been adjusted to properly reflect sample dilutions?	
9.3	Yes	No	N/A	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis.	

10.0 Field QA/QC

10.1	Yes	No	N/A	Were any rinsate blanks collected?	
10.2	Yes	No	N/A	Are target analytes present in the rinsate blank? List compounds present with concentration and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary.	

11.0 Application of Validation Qualifiers

Validation qualifiers should now be applied to any result pertaining to this method by recording the flags directly on the summary tables. Each time edits are made to the tables, reviewer will initial and date tables. A project narrative should be written upon completion of the data quality evaluation, but may not be necessary due to data use (e.g. internal use only). This narrative will address all qualifiers associated with each method

	Data Usable With Qualification
J	Estimated quantitation based upon QC data
B	Estimated quantitation possibly biased high or false positive based upon blank data
	Unusable Data
R	Data rejected based upon QC data
	Flagging Hierarchy
	R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

If at any time the reviewer is uncertain of the proper course of action when evaluating data, then that reviewer should consult with the Project Chemist or a Senior Chemist.

REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Inorganic Data Review, 1999".

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Initial Review by:_____Date:_____ SDG#_____
Senior Review by:_____Date:_____ Matrix_____

SUPPLEMENTAL NOTES

Section Heading

DQE ASTM D1552 Rev. 05/14/04
(Metabolic Fatty Acids)

Initial Review by:_____ Date:_____ SDG#_____
Senior Review by:_____ Date:_____ Matrix_____

DEFENSE DEPOT – MEMPHIS, TENNESSEE
DATA QUALITY EVALUATION
ASTM D1552
(Metabolic Fatty Acids)

Note: The following Data Quality Evaluation (DQE) for ASTM D1552 (metabolic fatty acids) as performed by Severn Trent Laboratory – Buffalo will be evaluated according to the labs QA/QC program. The COE Shell Document does not specifically address wet chemistry techniques.

1.0 Sample Integrity

					Notes
1.1	Yes ___	No ___	N/A ___	Was the project specific 28 day holding time met for metabolic fatty acids? Holding time is calculated as time elapsed from sampling to analysis. If not, flag results "J".	
1.4.1	Yes ___	No ___	N/A ___	Were the correct bottles and preservatives used upon collection of metabolic fatty acid samples? [40 mL VOA vials with no preservative @ 4° C]	
1.4.2	Yes ___	No ___	N/A ___	**Should DQE proceed? If no, apply "R" to metabolic fatty acid data results and proceed to next method in SDG.**	

2.0 Laboratory Method

2.1	Yes ___	No ___	N/A ___	Was the correct method used for analysis of metabolic fatty acids? [ASTM D1552]	
2.2	Yes ___	No ___	N/A ___	Were the quantitation limits in the SAP adhered to for all samples in this SDG except where dilutions were performed? Note any dilutions and/or results reported between the MDL and PQL. Results reported between the MDL and PQL are flagged "J"	

3.0 Initial and Continuing Calibration
Calibration information will be assumed to be within control for this method and will therefore not be further evaluated.

4.0 Method Blanks

4.1	Yes ___	No ___	N/A ___	Is the Method Blank summary present? Note SDG page number/s.	

Initial Review by:_____ Date:_____ SDG#_____
Senior Review by:_____ Date:_____ Matrix_____

					Notes
4.2	Yes ___	No ___	N/A ___	Was a Method Blank analyzed for each SDG or every 20 samples of similar matrix?	
4.3	Yes ___	No ___	N/A ___	Are all Method/Instrument/Reagent blanks less than the PQL? If not, lab should perform corrective action. List analyte and concentration present and apply the following : If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary	

5.0 Laboratory Control Standard (LCS)

5.1	Yes ___	No ___	N/A ___	Is the LCS and/or LCS duplicate summary form present? Note SDG page number/s.	
5.2	Yes ___	No ___	N/A ___	Was an LCS analyzed with each SDG or every 20 samples of similar matrix?	
5.3	Yes ___	No ___	N/A ___	Are spiked recoveries within laboratory limits in the LCS/LCSD? Flag results only **if both** the LCS and LCSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the LCS = J Hits and NDs that fail low in the LCS = J	

6.0 Matrix Spikes

6.1	Yes ___	No ___	N/A ___	Are the Matrix Spike/Matrix Spike Duplicate (MS/MSD) summary forms present? Note SDG page number/s.	
6.2	Yes ___	No ___	N/A ___	Were MS/MSDs analyzed at a frequency of 1 per 20 samples and if designated by project team, were proper samples spiked? If not list sample that was spiked.	
6.3	Yes ___	No ___	N/A ___	Were the recoveries of the MS/MSD within laboratory limits? Flag results only **if both** the MS and MSD recoveries were outside the limits. Flag Criteria: Hits in sample that fail high in the MS/MSD = J Hits and NDs that fail low in the MS/MSD = J	

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					Notes
6 4	Yes	No	N/A	Was the RPD between the MS/MSD < 20%? If not, flag results J.	

7.0 Duplicates

7 1	Yes	No	N/A	Were any intra-laboratory or field duplicates analyzed? At times the laboratory will choose samples at random for duplicate analysis as part of internal QA/QC. Record and cross-reference sample ID along with SDG page number/s.	
7.2	Yes	No	N/A	Is RPD between sample and duplicate < 20%? If not, list sample ID, concentration of both samples and RPD. Per USEPA National Functional Guidelines, "No action is taken based on percent difference of field duplicate sample data alone. However, using informed professional judgement, the data reviewer may use the field duplicate results in conjunction with other QC criteria to determine the need for some qualification of the data " Flag results J.	

8.0 Compound Quantitation and Reported Detection Limits

8.1	Yes	No	N/A	Are results present for all samples sent to the lab for metabolic fatty acids?	
8 2	Yes	No	N/A	Have PQLs been adjusted to properly reflect sample dilutions?	
8.3	Yes	No	N/A	Were all **reanalysis** data and reports submitted in the data package? Note any re-analysis and the reason for re-analysis.	

9.0 Field QA/QC

9 1	Yes	No	N/A	Were any rinsate blanks collected?	
9.2	Yes	No	N/A	Are target analytes present in the rinsate blank? List compounds present with concentration and apply the following rule. If sample concentration is ≤ 5x the blank value, assign a "B". If sample concentration is > 5x the blank value, no flag is necessary.	

10 0 Application of Validation Qualifiers

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R	Data rejected based upon QC data
	Flagging Hierarchy
	R > B > J

Final Note: Review this checklist for quality affecting items that may impact another SDG (e.g. samples run by same instrument on the same day or under the same calibration, etc.) Make some separate notes to reference when reviewing any other SDG affected to prevent redundancy in review.

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REFERENCES

USEPA Contract Laboratory Program, "National Functional Guidelines for Inorganic Data Review, 1999".

Initial Review by:_____Date:_____ SDG#_____
Senior Review by:_____Date:_____ Matrix_____

SUPPLEMENTAL NOTES

Section Heading

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FINAL PAGE

ADMINISTRATIVE RECORD

FINAL PAGE