Appendix C

CD-ROM Including: Laboratory Standard Operating Procedures

Legend Technical Services, St. Paul, MN
Braun Intertec, Minneapolis, MN
TestAmerica, West Sacramento, CA

(See CD included in Appendix B)

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: HEXAVALENT CHROMIUM (COLORIMETRIC)

SOP NO.: LABENV-035.5

Original Information		
Prepared by:	Brian Leigh	Date: 09/17/99
Technical Review:	Sharon Dahl	Date: 09/17/99
QA/QC Coordinator:		Date:
Authorized by:	Cheryl Sykora	Date: 09/17/99

Revision Information		
Supersedes:	LABENV-035.4	Date: 08/22/07
Revised by:	Cynthia Schultz	Date: 04/01/08
Signature:	______________________	Date: __________
Technical Review:	Jaime Zwers	Date: 04/01/08
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 04/04/08
Signature:	______________________	Date: __________

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Revision Information		
Supersedes:	LABENV-035.4	Date: 08/22/07
Revised by:	Cynthia Schultz	Date:
Signature:		Date:
Technical Review:	Jaime Zwers	Date:
Signature:		Date:
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 4/04/08

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FORM GEN-021 (05/07)

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: HEXAVALENT CHROMIUM (COLORIMETRIC)

SOP NO.: LABENV-035.5

Original Information		
Prepared by:	Brian Leigh	Date: 09/17/99
Technical Review:	Sharon Dahl	Date: 09/17/99
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Revision Information		
Supersedes:	LABENV-035.4	Date: 08/22/07
Revised by:	Cynthia Schultz	Date:
Signature:	[signature]	Date: 4/1/08
Technical Review:	Jaime Zwers	Date:
Signature:	[signature]	Date: 4/1/08
Authorized by:	Cheryl Sykora	Date:
Signature:		Date:

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FORM GEN-021 (05/07)

SOP TITLE: HEXAVALENT CHROMIUM (COLORIMETRIC)

1. PURPOSE

1.1 This document defines the procedure to be followed for the determination of hexavalent chromium in water and wastewater using diphenylcarbazide for color formation. The SOP is applicable to samples typically analyzed by Standard Methods (SM) 3500-Cr B, Online Version, 2001.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the standard operating procedure.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This method is applicable to water and wastewater samples only.

3.2 Hexavalent molybdenum and mercury salts can form color with the reagent, but concentrations of up to 200 mg/L of each can be tolerated.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 A lab coat and safety glasses should be worn.

4.4 When working with organic compounds, wear solvent resistant gloves.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Water samples should be collected in 250 mL unpreserved, plastic bottles and stored at 4 ± 2 °C.

5.4 The sample holding time, from collection to analysis, should not exceed 24 hours.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 Cary 50 BIO UV-VIS Spectrophotometer or equivalent

6.2 Cuvette with light path of 1 cm

6.3 Digestion vessels

6.4 0.45 µm plunge filter, or equivalent

6.5 Volumetric flasks, assorted volumes

6.6 Coloring reagent - dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone, store in a digest vessel, and discard when solution becomes discolored (should be a pale yellow color)

6.7 Concentrated sulfuric acid – ACS grade

6.8 Deionized (DI) water (>16.3 MΩ)

6.9 Chromium Calibration Standard – prepare one of the following:

6.9.1 500 µg/mL Standard – dissolve 141.4 mg $K_2Cr_2O_7$ in DI water and dilute to 100 mL

6.9.2 1000 ppm Standard – purchase commercially

6.10 Working Calibration Standard – prepare using one of the calibration standards above

6.10.1 Dilute 10 mL of the 500 µg/mL Chromium Calibration Standard to 1 L with DI water to produce a 5.0 µg/mL working standard

6.10.2 Dilute 5 mL of the 1000 ppm Chromium Calibration Standard to 1 L with DI water to produce a 5.0 µg/mL working standard

6.11 Second Source Standard – purchase a standard commercially, or prepare a reference standard, using a separate source than that used for calibration standards

7. PROCEDURE

7.1 Preparation of Water Samples

7.1.1 Prepare a Blank, LCS/LCSD, Calibration Verification Standard (CVS) and MS/MSD per batch of 20 samples or fewer.

7.1.1.1 The CVS is a mid-level standard and is required if a calibration curve is not analyzed. Recovery should be ± 10% of the true value or corrective action is taken.

7.1.1.2 Corrective action may include but is not limited to reanalyzing the standard, preparing and analyzing a new standard, preparing a new calibration curve, and/or using new reagents.

7.1.2 Pour at least 50 mL of each sample into a digestion vessel and filter with a 0.45 µm plunge filter. Blank, LCS/LCSD and CVS do not need to be filtered.

7.1.3 Label additional digestion vessels with the sample numbers and batch QC information.

7.1.4 Add 0.5 mL concentrated sulfuric acid to each digestion vessel.

7.1.5 Spike the LCS/LCSD and MS/MSD digestion vessels with 2.0 mL and the CVS digestion vessel with 2.5 mL of the Working Calibration Standard. Final concentrations will be 0.20 µg/mL and 0.25 µg/mL respectively.

7.1.6 Add the filtered sample to the 50 mL mark of the appropriate digestion vessel and mix well. Repeat for each sample, MS and MSD.

7.1.7 For the Blank, LCS/LCSD and CVS, add DI water to the 50 mL mark and mix well.

7.1.8 If the acidified sample is turbid or colored, prepare a second sample that will not have coloring reagent added to it.

7.1.9 Add 1.0 mL of the coloring reagent to the samples and QC and mix well. Allow 5-10 minutes for the color to develop.

7.2 Calibration

7.2.1 Prepare working standards at a minimum of 3 concentration levels, ranging from 0.020-0.50 ppm, by diluting the 5.0 µg/mL Working Calibration Standard with DI water and 0.5 mL of sulfuric acid to a final volume of 50 mL. A calibration blank must also be prepared using DI water. Add 1.0 mL of coloring reagent. A typical calibration curve would be:

Working Calib. Std. mL/50 mL	Conc. (µg/L)
0	0
0.20	20
1.0	100
2.5	250
5.0	500

7.2.2 Prepare a calibration curve of Concentration vs. Response. Correlation Coefficients should be 0.995 or greater.

7.2.3 A new standard curve will be run annually, at a minimum.

7.2.4 Calibration curve calculations are found in the QA Manual.

7.2.5 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.2.6 At the time of calibration, the Second Source Standard will be analyzed to verify calibration. The second source is processed the same as a sample.

7.2.6.1 Recovery should be ± 10% of the true value (unless limits are supplied by the vendor) or corrective action is taken.

7.2.6.2 Corrective action may include but is not limited to reanalyzing the second source, preparing and analyzing a new second source, preparing a new calibration curve, and/or using new reagents.

7.2.7 If the response for a peak exceeds the working range of the system or the highest standard, dilute the sample with DI water and reanalyze.

7.3 Analysis

7.3.1 Open the Cary software on the computer.

7.3.2 Go to 'File' and then 'Open Method'. Open the most recent Hexavalent Chromium method listed. Go to 'Setup' and enter sample labels. Be sure to include method blank, LCS, LCSD, MS, MSD and CVS.

7.3.3 If calibration standards were prepared, enter the number of standards and the standard concentrations.

7.3.4 Rinse out the cuvette twice with the method blank.

7.3.5 Fill the cuvette approximately ¾ full with method blank and wipe the sides clean with a Kimwipe™.

7.3.6 Place the cuvette into the spectrophotometer.

7.3.7 Using the computer mouse, click on the rectangle labeled 'Zero'.

7.3.8 Using the computer mouse, click on the rectangle labeled 'Start'.

7.3.9 When prompted for file name, enter the date of the analysis, Cr 6+, and the letter of the run. For example: 012204A Cr 6+. "A" for the first run of the day.

7.3.10 When prompted, select samples to be analyzed including standards if needed.

7.3.11 Analyze each sample as it is prompted (label given in step above will be used).

7.3.12 Between samples, rinse the cuvette twice with the next sample to be analyzed. Wipe the sides of the cuvette clean with a Kimwipe™.

7.3.13 If acidified sample is turbid or colored, take a reading of the colored and uncolored sample. Subtract the uncolored concentration from the colored concentration. Use this corrected concentration for the mg/L of hexavalent chromium in the sample.

7.3.14 If the response for an absorbance exceeds the working range of the system or the highest standard, prepare the sample at a dilution and re-analyze.

7.3.15 After analyzing all the samples, rinse the cuvette with deionized water.

7.3.16 If calibration standards were analyzed, save as a new calibration method (e.g. Cr 6+ 031208).

7.3.17 Print out the report and exit the software. Store printed report in the daily file.

7.3.18 Fill out the Cary 50 logbook.

7.4 Calculation

7.4.1 Calculate the concentration of the analyte in the sample using the following equation:

$$Cr^{6+}, mg/L = \frac{(C)(D)}{1000}$$

C = curve concentration in µg/L (prior to dilutions)
D = dilution factor

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, on an annual basis. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs values can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. The method blank must be less than the reporting limit or the sample batch is reanalyzed if possible. If it is not possible to reanalyze, the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Due to lack of samples analyzed, LCS accuracy limits are not generated in-house, but are set at 80.0-120%. LCS precision limits are set at ≤20%.

9.3.2 Due to lack of samples analyzed, MS accuracy limits are not generated in-house, but are set at 75.0-125%. MS precision limits are set at ≤20%.

9.3.3 QC calculations are found in the QA Manual.

9.3.4 LCS and MS are reviewed.

9.3.5 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is reanalyzed if possible. If the batch cannot be reanalyzed, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.6 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS is flagged and/or a case narrative is written.

10. REPORTING

10.1 Water sample results are reported in mg/L.

10.2 The reported result is rounded to two significant figures.

10.3 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limit and Reporting Limit

12. REFERENCES

12.1 Standard Methods for the Examination of Water and Wastewater, Method 3500-Cr B, Online Version, 2001

Appendix A

Initial Demonstration of Capability (IDC)
Hexavalent Chromium (Colorimetric)

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards in lab-grade water and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: 80.0-120%
   Precision: $\leq$ 20.0 %RPD

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limit and Reporting Limit
Hexavalent Chromium (Colorimetric)

Parameter	**Water MDL (mg/L)**	**Water RL (mg/L)**
Hexavalent chromium	0.0059	0.020

DOCUMENT REVIEW

DOCUMENT:	LABENV-035.5 SOP
REVIEWER:	Cynthia Schultz
DATE:	03/12/08

SECTION	CHANGES
7.3.13 & 7.3.14	Added sections
7.3.16	Added (e.g. Cr 6+ 031208)
7.3.17 & 7.3.18	Deleted sections of old SOP
Appendix B	Updated MDLs

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: ANIONS IN AQUEOUS AND SOLID SAMPLES BY ION CHROMATOGRAPHY

SOP NO.: LABENV-026.7

Original Information		
Prepared by:	Jennifer Nelson	Date: 03/12/96
Technical Review:		Date:
QA/QC Coordinator:	Sharon Cenis	Date: 03/28/96
Authorized by:	Cheryl Sykora	Date: 03/29/96

Revision Information		
Supersedes:	LABENV-026.6	Date: 04/04/08
Revised by:	Scott Creekmur	Date: 04/24/09
Signature:	______________	Date: ______
Technical Review:	Kelly French	Date: 04/24/09
Signature:	______________	Date: ______
Authorized by:	Cheryl Sykora	Date: 04/27/09
Signature:	______________	Date: ______

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SOP TITLE: ANIONS IN AQUEOUS AND SOLID SAMPLES BY ION CHROMATOGRAPHY

1. PURPOSE

1.1 This document defines the procedure to be followed for analysis of various anions in aqueous and solid samples by ion chromatography. The SOP is applicable to samples typically analyzed by a modified EPA Method 9056.

1.2 For all anions, 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 exchanger. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppressor 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.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the standard operating procedure.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This SOP is applicable to aqueous and solid samples.

3.2 Any species with a retention time similar to that of the desired ion will interfere. Large quantities of ions eluting close to the ion of interest will also result in an interference. Sample dilution and/or the use of the method of standard additions can also be used. For example, high levels of organic acids may be present in industrial wastes, which may interfere with inorganic anion analysis. Two common species, formate and acetate, elute between fluoride and chloride.

3.3 Slight variations in mobile phase buffer concentrations can effect the retention time of analytes. Initial calibration curves should be generated when a new batch of mobile phase is prepared.

3.4 Because bromide and nitrate elute very close together, they are potential interferences for each other. It is advisable not to have Br/NO_3 ratios higher than 1:10 or 10:1 if both anions are to be quantified. If nitrate is observed to be an interference with bromide, use of an alternate detector (e.g. electrochemical detector) is recommended.

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 baseline in ion chromatograms.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Water and solid samples may be collected in unpreserved plastic or glass bottles and stored at
4 ± 2 °C.

5.4 Method 9056 states to analyze the samples as soon as possible.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 HPLC system with data processing equipment

6.2 Waters 431 Conductivity Detector, or equivalent

6.3 Shodex IC SI-90G guard column, or equivalent

6.4 Shodex IC SI-90 4E column, or equivalent

6.5 Alltech suppressor cartridge, or equivalent

6.6 HPLC autosampler vials

6.7 Analytical balance, capable of measuring to 0.1 mg

6.8 Syringes - 0.5mL, 1.0mL and 5.0mL

6.9 3.0mL Disposable Syringes with Luer-Lok Tip

6.10 Whatman 0.2 µm Polyethersulfone Syringe Filter, or equivalent

6.11 HPLC grade water

6.12 Deionized (DI) Water (>16.3 MΩ)

6.13 Cleaned & Dried Ottawa Sand, or equivalent (Sonicate or rinse with DI before use to clean)

6.14 Sodium bicarbonate, 99.8% purity (CAS# 831-990)

6.15 Sodium carbonate, A.C.S. (CAS# 3506-01)

6.16 Whatman 0.45 µm Nylon Membrane filter, or equivalent

6.17 Whatman pH Test Strips, or equivalent

6.18 Merckquant Chloride test strips, or equivalent

6.19 EM Quant Sulfate test strips, or equivalent

6.20 Orion Nitrate/Nitrite test strips, or equivalent

6.21 Mobile Phase Stock Solution — Transfer 14.28 g sodium bicarbonate and 19.08 g sodium carbonate to a 1000 mL volumetric flask. Dilute to volume with HPLC grade water and mix to produce a 180 mM sodium carbonate, 170 mM sodium bicarbonate solution. This solution is stable for 6 months when stored in a refrigerator in a stoppered bottle.

6.22 Mobile Phase Working Solution — Pipette 10.0 mL of the Mobile Phase Stock Solution into a 1000 mL volumetric flask. Dilute to volume with HPLC grade water and mix to produce a 1.8 mM sodium carbonate and 1.7 mM sodium bicarbonate solution. Filter solution through a 0.45 µm membrane filter and degas by sonication for no less than 5 minutes. Prepare working solution weekly.

NOTE: Solution volumes may be modified, provided final concentrations are maintained.

6.23 Calibration Stock – Anion Mixture A (Alltech Cat# 26910200), or equivalent

6.23.1 Fluoride (F) = 10 mg/L

6.23.2 Chloride (Cl) = 20 mg/L

6.23.3 Nitrite (NO_2) = 20 mg/L

6.23.4 Bromide (Br) = 20 mg/L

6.23.5 Nitrate (NO_3) = 20 mg/L

6.23.6 Phosphate (PO_4) = 30 mg/L

6.23.7 Sulfate (SO_4) = 30 mg/L

6.24 Spiking Solution – Anion Mix 5 (Alltech Cat# 2691110), or equivalent

6.24.1 Fluoride (F) = 25 mg/L

6.24.2 Chloride (Cl) = 50 mg/L

6.24.3 Nitrite (NO_2) = 50 mg/L

6.24.4 Bromide (Br) = 50 mg/L

6.24.5 Nitrate (NO_3) = 50 mg/L

6.24.6 Phosphate (PO_4) = 50 mg/L

6.24.7 Sulfate (SO_4) = 50 mg/L

7. PROCEDURE

7.1 Preparation of Aqueous Samples

7.1.1 Use pH test strips to determine approximate sample pH. Dilute sample with HPLC grade water to acceptable pH range (pH 5-9 su). Adjusting the pH with acids or bases could cause interferences and should not be used.

7.1.2 Use test strips (e.g. Cl^-, SO_4^{2-}, NO_3^-/NO_2^-) as needed to determine if analyte concentration is outside of calibration range or if components in the sample matrix may cause interferences during the analysis.

7.1.3 Filter each sample through a 0.2 μm syringe filter into an HPLC vial.

7.1.4 A typical batch for environmental applications will have a blank, a laboratory control spike (LCS) and matrix spike/matrix spike duplicate (MS/MSD). A laboratory control spike/laboratory control spike duplicate (LCS/LCSD) will be substituted if enough sample is not provided.

7.1.5 A typical batch for industrial chemistry applications will have a blank and a LCS/LCSD.

7.1.6 For the preparation of the LCS/LCSD, combine 100 μL of Anion Mixture 5 and 900 μL of HPLC grade water in an HPLC vial and mix. Final concentration will be 2.5 mg/L for fluoride and 5.0 mg/L for the other anions.

7.1.7 For the preparation of the MS/MSD, combine 100 μL of Anion Mixture 5 and 900 μL of the sample selected for QC and mix. Final spiked concentration will be 2.5 mg/L for fluoride and 5.0 mg/L for the other anions.

7.2 Preparation of Solid Samples

7.2.1 Transfer 2.0 g of sample and 2.0 mL of DI water to a suitable container. If not enough sample is available, maintain a 1:1 sample:DI water ratio. Sonicate for 30 minutes and allow to stand 5 minutes after sonication to let solids settle. Filter liquid through a 0.2 μm syringe filter into an HPLC vial. Use a vial insert if the filtrate is less than 300 μL.

7.2.2 Prior to analysis, check filtrate with test strips to ensure dilutions are not required.

7.2.3 A typical batch for environmental applications will have a blank, laboratory control spike (LCS) and matrix spike/matrix spike duplicate (MS/MSD). A laboratory control spike/laboratory control spike duplicate (LCS/LCSD) will be substituted if enough sample is not provided.

7.2.4 A typical batch for industrial chemistry applications will have a blank and an LCS/LCSD.

7.2.5 For the blank, transfer 2.0 g of Ottawa sand and 2.0 mL of DI water to a suitable container. Sonicate for 30 minutes and allow to stand 5 minutes after sonication to let solids settle. Filter liquid through a 0.2 μm syringe filter into an HPLC vial.

7.2.6 For the preparation of the LCS/LCSD, transfer 2.0 g of Ottawa sand to a suitable container. Add 200 µL Anion Mixture 5 and 1.8 mL of DI water and mix. Sonicate for 30 minutes and allow to stand 5 minutes after sonication to let solids settle. Filter liquid through a 0.2 µm syringe filter into an HPLC vial. Final concentration will be 2.5 mg/kg for fluoride and 5.0 mg/kg for the other anions.

7.2.7 For the preparation of the MS/MSD, transfer two aliquots of 2.0 g of the sample selected for spiking to suitable containers. Add 200 µL Anion Mixture 5 and 1.8 mL of DI water to each and mix. Sonicate for 30 minutes and allow to stand 5 minutes after sonication to let solids settle. Filter liquid through a 0.2 µm syringe filter into an HPLC vial. Use a vial insert if the filtrate is less than approximately 300 µL. Final spiked concentration will be 2.5 mg/kg for fluoride and 5.0 mg/kg for the other anions.

7.3 Calibration

7.3.1 Prepare working standards at a minimum of 6 concentration levels by diluting Anions Mixture A and the 0.50 mg/L standard. Typical calibration curves would be:

Level	Anion A mL/1mL	L4 mL/1 mL	F	Cl	Br	NO_3	PO_4	SO_4
L1	------	0.10	0.50	1.0	1.0	1.0	1.5	1.5
L2	0.10	-----	1.0	2.0	2.0	2.0	3.0	3.0
L3	0.25	-----	2.5	5.0	5.0	5.0	7.5	7.5
L4	0.50	-----	5.0	10.0	10.0	10.0	15.0	15.0
L5	0.75	-----	7.5	15.0	15.0	15.0	22.5	22.5
L6	1.0	-----	10.0	20.0	20.0	20.0	30.0	30.0

NOTE: Solution volumes may be modified, provided final concentrations are maintained.

7.3.2 Prepare calibration curves of Concentration vs. Response. Correlation Coefficients should be 0.990 or greater.

7.3.3 Calibration curve calculations are found in the QA Manual.

7.3.4 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.4 Analysis

7.4.1 Recommended HPLC conditions

7.4.1.1 Mobile Phase – 1.8 mM sodium carbonate, 1.7 mM sodium bicarbonate

7.4.1.2 Flow Rate – 1.5 mL/min

7.4.1.3 Column Temp. – 25 ºC Ambient

7.4.1.4 Sample size – 20 µL

7.4.1.5 Detector – Conductivity

7.4.1.6 Base Range – 200 µS

7.4.2 A mid-level or calibration verification standard (CVS) is analyzed at the beginning of the run (if an initial calibration curve was not analyzed), after every twenty samples, and at the end of the run. Recoveries should be ± 10% or corrective action should be taken.

7.4.3 Corrective action may include reanalyzing the CVS and/or flagging the data in the daily file.

7.4.4 If the response for a peak exceeds the working range of the system or the highest standard, dilute the sample with water and re-analyze.

7.5 Calculation

7.5.1.1 Compute the concentration of the analyte in the sample using the following equation:

$$Concentration\ (mg/L) = (C)(D)$$

C = on-column, mg/L (prior to dilutions)
D = dilution factor

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

9. QA/QC

9.1 Method Blank

9.1.1 A method blank is analyzed with each batch of samples prepared at the same time. The method blank must be less than the reporting limit or the data will be flagged, where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.2 MDL, PQL, RL

9.2.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, on an annual basis. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDL and RL values can be found in Appendix B. Project specific RLs may override those listed.

9.3 Control Limits

9.3.1 Accuracy control limits are generated for LCS and MS. In-house control charts are generated semi-annually, using 20 Percent Recovery points, as follows:

9.3.1.1 Upper and Lower Control Limit = Mean ± 3s

9.3.1.2 Upper and Lower Warning Limit = Mean ± 2s

9.3.1.3 s = Standard deviation

9.3.2 Precision control limits are generated for LCS/LCSD and MS/MSD. In-house control charts are generated semi-annually, using 20 RPD points, as follows:

9.3.2.1 Control Limit = Mean + 3s

9.3.2.2 Warning Limit = Mean + 2s

9.3.2.3 s = Standard deviation

9.3.2.4 RPD = Relative Percent Difference

9.3.3 In-house limits are used for compliance, as the method does not list specific limits. The limits will be reviewed for reasonableness before being used within the laboratory.

9.3.3.1 In-house limits that calculate narrower than 85.0-115% are set to 85.0-115% (i.e. in-house limits = 87.8-116%, limits are set at 85.0-116%). In-house limits that calculate wider than 80.0-120% are set to 80.0-120% (i.e. in-house limits = 83.4-125%, limits are set at 83.4-120%).

9.3.3.2 In-house precision limits that calculate narrower than 15% RPD are set to 15% (i.e. in-house limits = 11.3%, limits are set at 15%). In-house precision limits that calculate wider than 20% are set to 20% (i.e. in-house limits = 28.5%, limits are set at 20%).

9.3.4 If in-house limits have not been established and 20 points are not collected within a year, accuracy limits are set at 85.0-115% and precision limits are set at ≤ 20% RPD.

9.3.5 QC calculations are found in the QA Manual

9.3.6 LCS and MS data are reviewed.

9.3.7 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is re-analyzed if possible. If the batch cannot be re-analyzed, the information is placed in the daily and project files, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.8 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS is flagged and/or a case narrative is written.

10. REPORTING

10.1 Aqueous sample results are reported in mg/L.

10.2 Solid sample results are reported in mg/kg on a dry weight basis.

10.3 The reported result is rounded to two significant figures.

10.4 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

12. REFERENCES

12.1 Manufacturer's Operating Manuals

12.2 EPA Method 9056

Appendix A

Initial Demonstration of Capability (IDC)
Anions in Solid and Aqueous Samples by IC

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards of all the parameters in Ottawa sand and/or lab-grade water and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: LCS limits
   Precision: LCS limits

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
Anions by IC

Parameter	Aqueous MDL (mg/L)	Aqueous RL (mg/L)	Solid MDL (mg/kg)	Solid RL (mg/kg)
Bromide	0.30	1.0	0.30	1.0
Chloride	0.17	1.0	0.17	1.0
Fluoride	0.13	0.50	0.13	0.50
Nitrate as NO_3	0.16	1.0	0.16	1.0
Nitrate as N (calculated)	0.037	0.23	0.037	0.23
Nitrite as NO_2	0.11	1.0	0.11	1.0
Nitrite as N (calculated)	0.033	0.30	0.033	0.30
Phosphate	0.42	2.1	0.42	2.1
Sulfate	0.26	1.5	0.26	1.5

DOCUMENT REVIEW

DOCUMENT:	SOP LABENV-026.7
REVIEWER:	Scott Creekmur
DATE:	01/20/09

SECTION	**CHANGE**	**RATIONALE**
6.8	Added ‘0.5mL, 1.0mL and 5.0mL’	New syringes purchased for improved accuracy
6.9	Added ‘3.0mL Disposable Syringes with Luer-Lok Tip’	Described tip-type for disposable syringes
6.13	Added “Cleaned & Dried”	Described needed cleaning of sand prior to use.
Appendix B	Updated MDLs	Annual update

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: MERCURY SAMPLE PREPARATION FOR COLD VAPOR GENERATION

SOP NO.: LABENV-037.8

Original Information		
Prepared by:	Lisa Bloomgren	Date: 01/18/02
Technical Review:		Date:
QA/QC Coordinator:	Terri Olson	Date: 02/26/02
Authorized by:	Cheryl Sykora	Date: 02/26/02

Revision Information		
Supersedes:	LABENV-037.7	Date: 04/04/08
Revised by:	Viktor Yakovlev	Date: 04/22/09
Signature:	______________________	Date: __________
Technical Review:	Tammika Shedd	Date: 04/22/09
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 04/27/09
Signature:	______________________	Date: __________

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LEGEND TECHNICAL SERVICES, INC.

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TITLE: MERCURY SAMPLE PREPARATION FOR COLD VAPOR GENERATION
SOP NO.: LABENV-037.8

Original Information		
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Authorized by:	Cheryl Sykora	Date: 02/26/02

Revision Information		
Supersedes:	LABENV-037.7	Date: 04/04/08
Revised by: Signature:	Viktor Yakovlev [signature]	Date: Date: 4/22/09
Technical Review: Signature:	Tammika Shedd [signature]	Date: Date: 04/22/09
Authorized by: Signature:	Cheryl Sykora [signature]	Date: Date: 4/27/09

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SOP TITLE: MERCURY SAMPLE PREPARATION FOR COLD VAPOR GENERATION

1. PURPOSE

1.1 This document defines the procedure to be followed for preparing samples to be analyzed for mercury by the cold vapor atomic absorption technique. The SOP is applicable to mercury samples typically analyzed by EPA 245.1, EPA 7470A, and EPA 7471A.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the SOP.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 Potassium permanganate is added to eliminate possible interferences from sulfide.

3.2 If the laboratory will be filtering the sample for dissolved mercury analysis, do not perform nitric acid preservation.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 Safety glasses and gloves should be worn when handling samples and reagents.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Water samples should be collected in a polyethylene or glass container and preserved with 1:1 nitric acid to a pH < 2.

5.4 If a water sample is received with pH > 2, it is preserved in the laboratory and allowed to sit for a minimum of 24 hours at which time the pH is re-tested. The addition of the acid is noted on the appropriate chain-of-custody. If pH < 2, proceed. If not, repeat until pH is < 2, if possible. Highly alkaline samples may need to be digested at a reduced volume with excess acid, rather than dilute the original sample in an attempt to lower the pH.

5.5 Document the final pH of all samples in the Digestion Log Book under “Comments.”

5.6 The recommended holding time for water samples is 28 days.

5.7 Solid samples should be collected in polyethylene or glass containers and stored at 4 ± 2 °C.

5.8 The recommended holding time for solid samples is 28 days.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 Top loading balance

6.2 Block digester

6.3 Digestion vessels

6.4 Plunge filters

6.5 Disposable pipets

6.6 Deionized (DI) water (>16.3 MΩ)

6.7 Nitric Acid (HNO_3), concentrated, trace metal grade

6.8 Hydrochloric acid (HCl), concentrated, trace metal grade

6.9 Aqua regia (3:1 HCl:HNO_3 solution) – prepare immediately before use

6.10 5% potassium permanganate solution

6.11 Hydroxylamine hydrochloride, reagent grade

6.12 Certified Calibration Stock Standard – 1000 ppm (two different lots numbers are used)

6.13 Intermediate Stock Standard 1 (ISS1) – dilute 2.5 mL of the 1000 ppm certified stock standard (first lot number) and 12.5 mL of Aqua Regia with DI water in a 250 mL volumetric flask to produce a 10 ppm solution

6.14 Intermediate Stock Standard 2 (ISS2) – dilute 2.5 mL of the 1000 ppm certified stock standard (second lot number) and 12.5 mL of Aqua Regia with DI water in a 250 mL volumetric flask to produce a 10 ppm solution

6.15 Mercury Working Standard Solution 1 (MWSS1) – dilute 5.0 mL of ISS1 and 25 mL of Aqua Regia with DI water in a 500 mL volumetric flask to produce a 0.10 ppm solution and use this solution for calibration (calibration standards range from 0.50 – 10 ppb), LCS, LCSD, MS, and MSD – the spike concentration for the LCS, LCSD, MS, and MSD is 2.0 ppb

6.16 Mercury Working Standard Solution 2 (MWSS2) – dilute 5.0 mL of ISS2 and 25 mL of Aqua Regia with DI water in a 500 mL volumetric flask to produce a 0.10 ppm solution and use this solution for the QC standard or second source – the concentration for the second source standard is 5.0 ppb

7. PROCEDURE

7.1 Fill out the appropriate information in the Digestion Log Book, including sample numbers to be prepared. Confirm sample ID and requested analyte information with the chain-of-custody (c-o-c).

7.2 For Quality Control (QC), indicate the prep batch # under the project # column for the Blank, Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD). The LCS is also referred to as the Laboratory Fortified Blank (LFB) or Blank Spike (BS). The prep batch number is obtained from the LIMS system. For Matrix Spike (MS) and Matrix Spike Duplicate (MSD), indicate the project and sample number in the appropriate columns. MS is also referred to as the Laboratory Fortified Matrix (LFM). A batch consists of no more than 20 samples. If less than 20 samples are in the batch, “Z” out the remaining spaces on that page, initial, and date.

7.3 Label digestion vessels with sample IDs. Label digestion vessels for the Blank, LCS, and LCSD including the batch number. Along with the sample ID, label MS for sample matrix spike and MSD for sample matrix spike duplicate.

7.4 Preparation of Water Samples

7.4.1 Shake all samples prior to transferring into digestion vessels.

7.4.2 Add 1.0 mL of MWSS1 to the digestion vessels labeled LCS, LCSD, MS, and MSD (obtaining a concentration of 2.0 ppb).

7.4.3 Dilute, with DI water, the blank, LCS, and LCSD to the 50 mL graduation on the digestion vessel. Dilute, with sample, the MS and MSD to the 50 mL graduation on the digestion vessel.

7.4.4 Measure 50 mL of each sample into its respective digestion vessel, using the graduations on the vessel.

7.4.5 Using a disposable pipet, add 2.5 mL of aqua regia to all the digestion vessels.

7.4.6 Add 5.0 mL of 5% potassium permanganate solution to each vessel. Less sample volume should be used if the potassium permanganate is significantly reduced before placing in block digester. Additional potassium permanganate may be used in conjunction with a lesser sample volume.

7.4.7 Loosely cover each digestion vessel with its cap. Place the samples, spikes, and blank in the block digester for 2 hours at 95 °C. Record the time in the Digestion Log Book.

7.4.8 Remove the samples from the block and allow them to cool. Record the time in the Digestion Log Book.

7.4.9 Add approximately 400 mg (~½ inch back on tip of spatula) of hydroxylamine hydrochloride to reduce the potassium permanganate, cap tightly and mix.

7.4.10 If sediment is present, filter the sample using a plunge filter. Also filter the QC at this point, including the Blank, LCS, and LCSD. If samples are not being filtered, the QC does not need to be filtered.

7.5 Preparation of TCLP Samples

7.5.1 Shake all samples prior to transferring into digestion vessels.

7.5.2 Add 1.0 mL of MWSS1 to the digestion vessels labeled LCS, LCSD, MS, and MSD (obtaining a concentration of 2.0 ppb).

7.5.3 Add 10 mL of the TCLP leachate blank to the batch Blank, LCS and LCSD samples.

7.5.4 Add 10 mL of each TCLP sample to the appropriate digestion vessel.

7.5.5 Dilute, with DI water, all samples including the Blank, LCS, and LCSD to the 50 mL graduation on the digestion vessel.

7.5.6 Using a disposable pipet, add 2.5 mL of aqua regia to all the digestion vessels.

7.5.7 Add 5.0 mL of 5% potassium permanganate solution to each vessel. Less sample volume should be used if the potassium permanganate is significantly reduced before placing in block digester. Additional potassium permanganate may be used in conjunction with a lesser sample volume.

7.5.8 Loosely cover each digestion vessel with its cap. Place the samples, spikes, and blank in the block digester for 2 hours at 95 °C. Record the time in the Digestion Log Book.

7.5.9 Remove the samples from the block and allow them to cool. Record the time in the Digestion Log Book.

7.5.10 Add approximately 400 mg (~½ inch back on tip of spatula) of hydroxylamine hydrochloride to reduce the potassium permanganate, cap tightly and mix.

7.5.11 If sediment is present, filter the sample using a plunge filter. Also filter the QC at this point, including the Blank, LCS, and LCSD. If samples are not being filtered, the QC does not need to be filtered.

7.6 Preparation of Solid Samples

7.6.1 Weigh out 0.50 grams of the solid samples and place in their respective digest vessel. For one of the solid samples, weigh out two additional aliquots, one for the MS and one for the MSD. Record the actual weights in the Digestion Log Book and LIMS.

7.6.2 Add 1.0 mL of MWSS1 to the digestion vessels labeled LCS, LCSD, MS, and MSD (obtaining a concentration of 2.0 ppb).

7.6.3 Using a disposable pipet, add 2.5 mL of aqua regia to all the digestion vessels.

7.6.4 Dilute the samples, blank, LCS, LCSD, MS, and MSD with DI water to the 50 mL graduation and then add an extra 2.5 mL of DI water.

7.6.5 Add 5.0 mL of the 5% potassium permanganate solution to each vessel. Each vessel should now have a volume of 57.5 mL.

7.6.6 If the potassium permanganate is significantly reduced before placing in the block digester, the sample should be re-prepped with additional potassium permanganate ensuring final volume is 57.5 mL.

7.6.7 Loosely cover each digestion vessel with its cap. Place the samples, spikes, and blank in the block digester for 30 minutes at 95 °C. Record the time in the Digestion Log Book.

7.6.8 Remove the samples from the block and allow them to cool. Record the time in the Digestion Log Book.

7.6.9 Add approximately 400 mg (~½ inch back on tip of spatula) of hydroxylamine hydrochloride to reduce the potassium permanganate, cap tightly and mix.

7.6.10 Filter samples including the blank, LCS, and LCSD using the plunge filters.

7.7 Calibration, analysis and calculation are not applicable to this SOP but are addressed in the appropriate analytical SOP.

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

8.2 Highly contaminated samples are returned to the client for disposal.

9. QA/QC

9.1 Follow the QA/QC protocol outlined in the appropriate analytical SOP.

10. REPORTING

Not applicable

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

12. REFERENCES

12.1 EPA Methods 245.1, 7470A, and 7471A

Appendix A

Initial Demonstration of Capability (IDC)
Mercury Sample Preparation for Cold Vapor Generation

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: 245.1 = 85.0-115%, 7470A/7471A – 80.0-120% (245.1/7470A may be combined if tighter limits are used for acceptance)
   Precision: 245.1/7470A/7471A = ≤ 20 % RPD

7. The reagent blank must be less than the reporting limit (RL).

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

DOCUMENT REVIEW

DOCUMENT:	SOP LABENV-037.8
REVIEWER:	Viktor Yakovlev
DATE:	02/05/09

SECTION	CHANGE	RATIONALE
Document Review	Updated form	Revised form

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF NITROAROMATICS, NITRAMINES, AND PETN IN SOIL BY HPLC
SOP NO.: **LABENV-036.5**

Original Information		
Prepared by:	Tom Barrett	Date: 09/17/99
Technical Review:		Date:
Technical Director:		Date:
QA/QC Coordinator:	Sharon Dahl	Date: 09/17/99
Authorized by:	Cheryl Sykora	Date: 09/17/99

Revision Information		
Supersedes:	LABENV-036.4	Date: 11/28/05
Revised By:	Scott Creekmur	Date: 02/20/07
Signature:	______________________	Date: __________
Technical Review:	Erica Nastrom	Date: 02/20/07
Signature:	______________________	Date: __________

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FORM GEN-021 (02/07)

SOP TITLE: DETERMINATION OF NITROAROMATICS, NITRAMINES, AND PETN IN SOIL BY HPLC

1. PURPOSE

1.1 This document defines the procedure to be followed for the determination of nitroaromatics, nitramines, and PETN in soil and solids by HPLC using a photo diode array (PDA) detector. The SOP is applicable to samples typically analyzed by a modified EPA 8330.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the standard operating procedure.

2.3 An analyst trained by LEGEND Technical Services, Inc. shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 The procedure is limited to soil and solid samples.

3.2 Degradation products of tetryl appear as a shoulder on the 2,4,6-Trinitrotoluene peak. Peak heights rather than peak areas should be used when tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-Trinitrotoluene.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 When working with organic compounds, wear solvent resistant gloves.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Soil samples should be collected in unweighed 4 oz. glass jars with Teflon lined caps and stored at 4 ± 2 °C. Samples must be protected from light.

5.4 The recommended holding time for soil samples is 14 days until extraction and analysis within 40 days of extraction.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 HPLC with photodiode array detector (PDA)

6.2 Restek Ultra C-18 column 25 cm x 4.6 mm x 5 μm, or equivalent

6.3 Balance – capable of reading 0.1 g

6.4 Ultrasonic sonicator

6.5 Chiller

6.6 10 mL amber serum vials

6.7 Amber autosampler vials – 2 mL

6.8 Acrodisc (0.45 μm) – PTFE, or equivalent

6.9 Disposable Syringes – 3 mL, or equivalent

6.10 Disposable pipettes – 1.0 mL, or equivalent

6.11 Sand – Ottawa, or equivalent

6.12 Reagent water

6.13 Acetonitrile (ACN), HPLC grade

6.14 Methanol (MeOH), HPLC grade

6.15 Calcium chloride ($CaCl_2$), 50 g/L solution - dissolve 5 grams of calcium chloride in approximately 70 mL of reagent water; bring to a final volume of 100 mL with reagent water and mix well

6.16 8330 Calibration/Spike Stock – 1,000 ppm EPA 8330 Kit, Restek #31450 and #31451, or equivalent

6.17 PETN Calibration/Spike Stock – 1,000 ppm PETN, Restek #31600, or equivalent

6.18 Surrogate Stock – 1,000 ppm 1,2-dinitrobenzene Restek #31453, or equivalent

6.19 Second Source 8330 Stock – 1,000 ppm, different vendor or different lot number than stock used for calibration

6.20 Second Source PETN Stock – 1,000 ppm, different vendor or different lot number than stock used for calibration

6.21 Second Source Surrogate Stock – 1,000 ppm, different vendor or different lot number than stock used for calibration

6.22 8330/PETN Continuing Calibration (CCAL) Intermediate Solution – dilute 50 µL each of the 1,000 ppm Second Source 8330 Stock, 1,000 ppm Second Source PETN Stock and 1,000 ppm Second Source Surrogate Stock to 10 mL with acetonitrile to produce a 5,000 ng/mL 8330/PETN Continuing Calibration (CCAL) Intermediate Solution

6.23 8330 Spike Working Solution – dilute 1.0 mL each of the 1,000 ppm 8330 Calibration/Spike Stock and the 1,000 ppm PETN Calibration/Spike Stock to 25 mL with acetonitrile to produce a 40 ppm 8330 Spike Working Solution

6.24 Surrogate Working Solution – dilute 1.0 mL of the 1,000 ppm Surrogate Stock to 25 mL with acetonitrile to produce a 40 ppm Surrogate Working Solution

7. PROCEDURE

7.1 Preparation of Samples

7.1.1 Weigh 2.0 g of sand into two 10 mL serum vials for the method blank and Laboratory Control Spike (LCS).

7.1.2 Weigh 2.0 g of each sample into a 10 mL serum vial. In each analytical batch, choose a sample and weigh out two additional aliquots, one for the Matrix Spike (MS) and one for the Matrix Spike Duplicate (MSD).

7.1.3 Add 0.5 mL of the 40 ppm Surrogate Working Solution to each sample, blank, LCS, and MS/MSD.

7.1.4 For the samples in each analytical batch selected for spiking, add 0.5 mL of the 40 ppm 8330 Spike Working Solution. A typical batch will have an LCS and MS/MSD (an LCS/LCSD will be substituted if insufficient sample is provided).

7.1.5 Add 4.5 mL of HPLC grade acetonitrile to the Blank and samples and 4.0 mL to the LCS and MS/MSD and close the vial with Teflon lined closure.

7.1.6 Place all the vials in a cooled ultrasonic bath (at or below 0°C) for 18 hours.

7.1.7 After 18 hours, remove all the vials and let them stand for 15 minutes to settle.

7.1.8 Combine 500 µL of the extract and 500 µL of the calcium chloride solution to create a 1:1 solution and mix thoroughly. Filter the 1:1 solution through a 0.45 µm PTFE acrodisc and place the filtrate in an autosampler vial

7.1.9 The resulting surrogate and spike concentrations will be 2000 ng/mL.

7.1.10 Retain the remainder of the extract in a Teflon capped vial.

7.2 Calibration

7.2.1 Prepare working standards at a minimum of five concentration levels, ranging from 500 – 7,500 ng/mL, by diluting the 1000 ppm 8330 Calibration/Spike Stock and the 1000 ppm PETN Calibration/Spike Stock with acetonitrile. For each calibration stock solution, combine 500 µL with 500 µL of calcium chloride to create a 1:1 solution, mix thoroughly and filter through a 0.45 µm acrodisc into an autosampler vial. A typical calibration curve would be:

Calibration Stock µL/10 mL	$CaCl_2$ Dil. Conc. ng/mL
10	500
20	1,000
50	2,500
100	5,000
150	7,500

7.2.2 The average response factor should be calculated for each analyte. The percent relative standard deviation (%RSD) should be less than 20% for each analyte. If the RSD for any analyte is greater than 20%, review the results (area counts, response factors, and RSD) for those analytes to ensure that the problem is not associated with just one of the calibration standards.

7.2.3 If the problem appears to be associated with a single standard, reprep and/or reanalyze that standard and calculate the RSD again.

7.2.4 If the %RSD is still greater than 20%, construct calibration curves of area versus concentration using a first order or linear fit. Correlation coefficients should be 0.990 or greater.

7.2.5 Calibration curve calculations are found in the QA Manual.

7.2.6 Reporting limit verification (RLV) is checked with each calibration curve by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or flagging data.

7.2.7 All extracts should be stored in the refrigerator in the dark.

7.3 Analysis

7.3.1 HPLC Conditions

7.3.1.1 Restek Ultra C-18 column

7.3.1.2 HPLC Mobile Phase - 44:56 H20:MeOH

7.3.1.3 Oven temperature 30 °C

7.3.1.4 PDA Wavelength 254nm for the typical 8330 list, 205nm for PETN

7.3.1.5 Flow Rate 1.0mL/min, run time 25min, isocratic

7.3.1.6 Injection volume 50 µL

7.3.2 Sample peak identification will be confirmed by peak retention time and peak spectrum as compared to standards.

7.3.3 If the response for a peak exceeds the working range of the system or the highest standard, dilute the extract with acetonitrile and re-analyze.

7.3.4 Prepare the CCAL by combining 500 µL of the 8330/PETN Continuing Calibration (CCAL) Intermediate Solution and 500 µL of the calcium chloride solution to create a 1:1 solution and mix thoroughly. Filter the 1:1 solution through a 0.45 µm PTFE acrodisc into an autosampler vial. The final concentrations of the 8330 compounds, PETN, and surrogate are 2,500 ng/mL.

7.3.5 The CCAL is analyzed at the beginning of the run in triplicate (if an initial calibration curve was not analyzed), after every ten samples (singly), and at the end of the run (singly). Recoveries for the triplicates should be ± 15% of the initial curve or corrective action should be taken. Recoveries for the continuing and end CCAL should be ± 15% of the triplicate average.

7.3.6 Corrective action may include reanalyzing the CCAL and/or flagging the data in the daily file.

7.4 Calculation

7.4.1 Computer software calculates the concentration of the sample based on the response. The calculation yields the final result in µg/g, which is equal to mg/kg.

$$Explosives\ (mg/kg) = \frac{(F)(CC)(V)}{(g)(1000)}$$

F = $CaCl_2$ curve factor (0.5 mL std/1.0 mL final volume = 2)
CC = concentration on column (ng/mL)
V = final volume (mL)
g = amount of soil (g)

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

8.2 Highly contaminated samples are returned to the client for disposal.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, when there is a change in the test method that may affect how the test is performed or when there is a major change in instrumentation. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. The method blank must be less than the reporting limit or the sample batch is re-analyzed, if possible. If it is not possible to re-analyze, the data will be flagged where appropriate. Do not subtract analytes in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Accuracy control limits are set at 70.0-130% for LCS, MS and surrogates.

9.3.2 Precision control limits are set at 20.0% RPD (relative percent difference) for LCS/LCSD and MS/MSD.

9.3.3 QC calculations are found in the QA Manual.

9.3.4 LCS, MS and surrogates are reviewed.

9.3.5 If the LCS data are outside the limits, the sample batch is re-extracted and/or re-analyzed if possible. If the batch cannot be re-analyzed, the information is placed in the daily and project files, and a case narrative is written for all client reports within the batch.

9.3.6 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS may be flagged in the case narrative of the report.

9.3.7 If a sample surrogate is outside the limits, the sample is re-extracted and/or reanalyzed if possible. If the sample cannot be re-extracted and/or reanalyzed, the data is flagged next to the actual result in the report.

10. REPORTING

10.1 Soil samples results are reported in mg/kg on a dry weight basis.

10.2 The reported result is rounded to two significant figures.

10.3 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

12. REFERENCES

12.1 EPA Method 8000B

12.2 EPA Method 8330

Appendix A

Initial Demonstration of Capability (IDC)
Determination of Nitroaromatics and Nitramines

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards in Ottowa sand, and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form ‘IDC 4 rep with RPD’, the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: LCS limits (70.0-130%)
   Precision: LCS limits (≤ 20% RPD)

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee’s personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
Nitroaromatics and Nitramines – EPA Method 8330(M)

Parameter	Soil MDL (mg/kg)	Soil RL (mg/kg)
1,3,5-Trinitrobenzene	0.15	3.0
1,3-Dinitrobenzene	0.084	3.0
2,4,6-Trinitrotoluene	0.18	3.0
2,4-Dinitrotoluene	0.063	3.0
2,6-Dinitrotoluene	0.13	3.0
2-Amino-4,6-dinitrotoluene	0.24	3.0
2-Nitrotoluene	0.59	6.0
3-Nitrotoluene	0.46	3.0
4-Amino-2,6-dinitrotoluene	0.27	3.0
4-Nitrotoluene	0.81	3.0
HMX	0.26	3.0
Nitrobenzene	0.11	3.0
RDX	0.15	3.0
Tetryl	0.50	3.0
PETN	0.60	3.0

DOCUMENT REVIEW

DOCUMENT:	LABENV-036.5 SOP
REVIEWER:	Scott Creekmur
DATE:	02/20/07

SECTION	**CHANGES**
6.2	Changed ‘Supelcosil LC-8 column’ to ‘Restek Ultra C-18 Column’
6.3	Removed ‘Supelcosil LC-PAH column’, resulted in renumbering of section
6.9	Added ‘Disposable’ and ‘or equivalent’
6.15	Deleted ‘Isopropyl Alcohol (IPA)
6.16	Changed ‘Supelco’ to ‘Restek’
6.17	Changed ‘Supelco’ to ‘Restek’
6.18	Added ‘Restek # 31453, or equivalent’
6.20	Added ‘PETN Second Source Stock – 1000 ppm, different vendor or different lot number’
6.21	Added ‘Second Source Surrogate Stock – 1,000 ppm, different vendor or different lot number than stock used for calibration
6.22	Added prep of ‘8330/PETN Continuing Calibration (CCAL) Intermediate Solution’
6.23	Revised the 8330 Spike Working Solution prep instructions
6.24	Revised the Surrogate Working Solution prep instructions
7.1.2	Changed ‘For one of the water samples’ to ‘In each analytical batch choose a sample and’
7.1.3	Changed ‘1.00 to 0.5’
7.1.4	Changed ‘1.00 to 0.5’
7.1.5	Changed ‘5’ to ‘4.5’ and added ‘to the Blank and samples and 4.0 mL to the LCS and MS/MSD’
7.1.6	Deleted
7.1.8-7.1.9	Combined 7.1.9 and 7.1.10 to ‘Combine 500 µL of the extract and 500 µL of the calcium chloride solution to create a 1:1 solution and mix thoroughly. Filter the 1:1 solution through a 0.45 µm acrodisc into an autosampler vial.
7.1.9	Deleted and added ‘The resulting surrogate and spike concentrations will be 2000 ng/mL’
7.1.10	Deleted ‘for HPLC analysis’

DOCUMENT REVIEW

DOCUMENT:	LABENV-036.5 SOP
REVIEWER:	Scott Creekmur
DATE:	02/20/07

SECTION	CHANGES
7.2 (previous SOP)	Deleted 'Preparation of Samples (PETN)' section
7.2.1	Revised preparation of working standards
7.4 (previous SOP)	Deleted 'Calibration (PETN)' section
7.2.2-7.2.3	Deleted calibration calculations
7.2.5	Added 'Calibration curve calculations are found in the QA Manual'
7.2.6	Added RLV statement
7.3.1	Revised HPLC conditions
7.3.2	Deleted confirmation HPLC conditions and added 'Sample peak identification will be confirmed by peak retention time and peak spectrum as compared to standards'
7.3.4	Added prep of CCAL
7.3.7	Deleted 'Any positive detection above the RL is compared with a spectral library for confirmation'
7.4	Changed the 'V = additive volume of…' in the calculation to 'V = final volume"
7.7 (previous SOP)	Deleted 'Calculation PETN' section
9.3.3	Added 'QC calculations are found in the QA Manual'
Appendix B	Updated MDLs; separated 2-nitrotoluene and 4-nitrotoluene
Cover Page	Updated to new form
SOP Form	Updated to new form with current address

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF ORGANOCHLORINATED PESTICIDES IN SOIL AND WATER SAMPLES

SOP NO.: LABENV-025.6

Original Information		
Prepared by:	Jennifer Nelson	Date: 11/03/95
Technical Review:		Date:
QA/QC Coordinator:	Sharon Cenis	Date: 03/28/96
Authorized by:	Cheryl Sykora	Date: 03/29/96

Revision Information		
Supersedes:	LABENV-025.5	Date: 01/02/08
Revised by:	Erin Hilton	Date: 06/11/08
Signature:	______________________	Date: __________
Technical Review:	Van Pham	Date: 06/11/08
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 06/11/08
Signature:	______________________	Date: __________

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Supersedes:	LABENV-025.5	Date: 01/02/08
Revised by:	Erin Hilton	Date:
Signature:	Erin A. Hilton	Date: 6/11/08
Technical Review:	Van Pham	Date:
Signature:	Van Pham	Date: 6/11/08
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 6/11/08

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SOP TITLE: DETERMINATION OF ORGANOCHLORINATED PESTICIDES IN SOIL AND WATER SAMPLES

1. PURPOSE

1.1 This document defines the procedure to be followed for the preparation and analysis for organochlorine pesticides in soil and water by gas chromatography (GC) using an electron capture detector (ECD). The SOP is applicable to samples typically analyzed by EPA Method 8081A.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the standard operating procedure.

2.3 An analyst experienced in GC techniques and trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This method is applicable to solid, wastewater, groundwater, and aqueous samples.

3.2 The Sonication Method may be used when a sample has the potential to be detrimental to the ASE (tar samples, fine sediments, etc.).

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 A lab coat and safety glasses should be worn.

4.4 When working with organic compounds, wear solvent resistant gloves.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Water samples should be collected in 1L amber bottles with Teflon lined caps and stored at 4 ± 2 °C.

5.4 The recommended holding time for water samples is 7 days until extraction and analysis within 40 days of extraction.

5.5 Soil samples should be collected in unweighed 4 oz. glass jars with Teflon lined caps and stored at 4 ± 2 °C.

5.6 The recommended holding time for soil samples is 14 days until extraction and analysis within 40 days of extraction.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 Gas chromatograph equipped with dual injectors, dual ECDs, and a data processing system

6.2 GC columns – Rtx®-CLPesticides™, 30 m x 0.32 mm, 0.5 µm film (Restek #11139), and Rtx®-CLPesticidesII™, 30 m x 0.32 mm, 0.25 µm film (Restek #11324) or equivalent. Whichever two columns are selected, they must be of dissimilar stationary phases.

6.3 Two liter Teflon separatory funnel, or equivalent

6.4 500 mL Kuderna Danish (K-D) flask

6.5 Steam bath

6.6 100 mm glass funnel

6.7 10 mL K-D concentrator

6.8 Snyder column

6.9 pH paper (0-14 Std. Units)

6.10 Graduated cylinder, 1000 mL

6.11 Volumetric flasks, 50 mL, 25 mL, 10 mL

6.12 Microliter syringes

6.13 Disposable glass pasteur pipets and bulb

6.14 Turbo Vap II and associated parts and glassware

6.15 Accelerated Solvent Extractor (ASE) and associated parts and glassware

6.16 Assorted laboratory glassware

6.17 Glass wool

6.18 2 mL autosampler vials

6.19 PTFE solvent rinsed boiling beads, or equivalent

6.20 Disposable weighing aluminum dishes – prerinsed with hexane and methylene chloride

6.21 Disposable graduated pipets

6.22 1 dram saver vials with Teflon liners

6.23 Anhydrous Sodium Sulfate (Na_2SO_4) - muffle at 400 °C for four hours before using

6.24 Sodium Hydroxide (NaOH) – reagent grade

6.25 10N Sodium Hydroxide – dissolve 40 g of the reagent grade NaOH in 100 mL organic free water

6.26 Sulfuric Acid (H_2SO_4) – reagent grade

6.27 1:1 Sulfuric Acid – slowly add 50 mL of the reagent grade H_2SO_4 to 50 mL organic free water

6.28 Hydromatrix® or equivalent – muffle at 400 °C for four hours before using

6.29 Ottawa Sand (20-30 mesh) or equivalent – muffle at 400 °C for four hours before using

6.30 Organic free water

6.31 Methylene chloride (CH_2Cl_2) - pesticide grade, or equivalent

6.32 Acetone – pesticide grade, or equivalent

6.33 Hexane – pesticide grade, or equivalent

6.34 Extraction Solvent Mix for Solids – 3:1 Hexane and Acetone

6.35 Pesticide Stock 1 – 2000 µg/mL, Supelco #47426-U or equivalent

6.36 Pesticide Stock 2 – 2000 µg/mL, Restek #32415 or equivalent, must be a different vendor or lot number than Pesticide Stock 1 (used in Pesticide Second Source Standard Solution)

6.37 Surrogate Stock – Restek #32000, 200 µg/mL for each of the following compounds: 2,4,5,6-Tetrachloro-m-xylene (TCMX), and Decachlorobiphenyl (DCB)

6.38 Toxaphene Stock – 1000 µg/mL, Supelco #4-8103 or equivalent

6.39 4,4-DDT and Endrin Breakdown Stock – 100 µg/mL each, Restek #32093 or equivalent

6.40 Pesticide Intermediate Solution – dilute 50 µL of 2000 µg/mL Pesticide Stock 1 and 500 µL of the 200 µg/mL Surrogate Stock into a 10 mL volumetric flask with hexane to produce a 10 µg/mL Pesticide and Surrogate Standard. Store in a freezer for up to six months.

6.41 Pesticide Spike Intermediate Solution – dilute 125 µL of the 2,000 µg/mL Pesticide Stock 1 into a 10 mL volumetric flask with 1:1 hexane:acetone to produce a 25 µg/mL Pesticide Spike Intermediate Solution. Store in a freezer for up to six months.

6.42 Pesticide Spike Standard – dilute 1.25 mL of the 25 µg/mL Pesticide Spike Intermediate Solution into a 25 mL volumetric flask with 1:1 hexane:acetone to produce a 1.25 µg/mL Pesticide Spike Standard. Store in a freezer for up to six months.

6.43 Surrogate Standard – dilute 250 µL of the 200 µg/mL Surrogate Stock into a 50 mL volumetric flask with 1:1 hexane:acetone to produce a 1.0 µg/mL Working Surrogate Standard. Store in a freezer for up to six months.

6.44 Toxaphene Intermediate Solution – dilute 10 µL of the 1,000 µg/mL Toxaphene Stock into a 10 mL volumetric flask with hexane to produce a 1.0 µg/mL Toxaphene Intermediate Solution. Store in a freezer for up to six months.

6.45 4,4'-DDT and Endrin Breakdown Standard – dilute 1-2 drops of the 100 µg/mL 4,4-DDT and Endrin Breakdown Stock with approximately 50 mL of hexane to produce the 4,4'-DDT and Endrin Breakdown Standard. Store in a freezer for up to six months.

NOTE: The actual concentration of the breakdown standard is not needed; the calculation uses responses only.

6.46 Pesticide Second Source Standard (CCAL/CCVS) – dilute 5 µL of the 2,000 µg/mL Pesticide Stock 2 and 50 µL of the 200 µg/mL Surrogate Stock to 50 mL with hexane to produce a 0.20 µg/mL Pesticide and Surrogate Second Source Standard. Store in a freezer for up to six months.

7. PROCEDURE

7.1 Preparation of Water Samples

7.1.1 Pre-rinse all glassware once with acetone, once with hexane, and three times with methylene chloride.

7.1.2 Mark the water level on the outside of bottle for later determination of volume.

7.1.3 Measure the pH of the sample and transfer to a pre-rinsed 2 L Teflon separatory funnel. (NOTE: If an evident layer of sediment is present, decant the sample and record on the extraction sheet.) The pH should be 5 - 9. If not, adjust the sample by using 10N NaOH or 1:1 H_2SO_4 and note on the extraction sheet.

7.1.4 Add 1.0 mL of the 1.0 µg/mL Surrogate Standard to all samples and QC. The final concentration will be 1.0 µg/L.

7.1.5 Add 1.0 mL of the 1.25 µg/mL Pesticide Spike Standard to samples selected for pesticide spiking. The final concentration will be 1.25 µg/L.

7.1.6 A typical batch will have an LCS and MS/MSD. An LCSD will be substituted if enough sample is not provided for a MSD.

7.1.7 Add approximately 60 mL methylene chloride to the sample bottle and rinse. Transfer to the separatory funnel with the sample. (NOTE: If the sample was decanted, add 60 mL of methylene chloride directly to the separatory funnel.)

7.1.8 Cap and shake vigorously for 10 seconds, and then vent. Cap and shake for two minutes. Allow the methylene chloride to separate from the sample.

7.1.8.1 If an emulsion interface between the layers is more than one-third the size of the solvent layer, the analyst should perform a beaker break without the use of Na_2SO_4.

7.1.8.2 Rinse the beaker with methylene chloride and quantitatively transfer. Drain the solvent layer into a glass 100 mm funnel containing a glass wool plug and about 2-3 inches of anhydrous muffled Na_2SO_4. Rinse funnel with methylene chloride.

7.1.9 Drain into a 500 mL K-D flask equipped with a 10 mL K-D concentrator for Nitrogen Blowdown.

7.1.10 Repeat with two additional fresh portions of methylene chloride.

7.1.11 After the final extraction, rinse the sodium sulfate with 20-30 mL of methylene chloride to complete the quantitative transfer.

7.1.12 If the emulsion layer is still present after the final shake, the analyst should employ mechanical techniques to complete the phase separation. Refer to the protocol found in Work Instruction (WI) 'Handling Emulsions'.

7.1.13 Fill sample bottle with tap water to mark made previously. Transfer to a graduated cylinder and record volume on extraction sheet.

7.1.14 K-D Technique / Nitrogen Blowdown

7.1.14.1 Add one solvent rinsed boiling bead to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-85 °C) so that the K-D concentrator is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot vapor. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 20 mL, add 20 mL of hexane through the Snyder column.

7.1.14.2 Concentrate to approximately 5 mL, remove the K-D apparatus from the steam bath, and allow it to cool. Remove the Snyder column.

7.1.14.3 Put the concentrator tube in a warm bath (about 35°C) and evaporate the solvent volume to less than 5 mL using a gentle stream of clean, dry nitrogen. During evaporation, the tube solvent level must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Do not allow the extract to go dry. Using a disposable pipet, adjust the final volume to 5.0 mL with hexane and mix the extract completely.

7.1.14.4 Transfer approximately 1 mL to a 2 mL autosampler vial and put the rest in a 4 mL saver vial. Store in freezer until analysis.

7.2 Preparation of Soil Samples – ASE technique

7.2.1 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

7.2.2 Place 2 filters paper on top of the open end of the cell body. Use the black cylindrical insertion tool to push filter to the bottom of the assembled cell body. Very fine soils may require three filters.

7.2.3 Use a 1:1 Ottawa Sand:Hydromatrix® mixture for the blank and Laboratory Control Sample (LCS). A typical batch will have an LCS and MS/MSD. LCS/LCSD will be substituted if enough sample is not provided.

7.2.4 Weigh approximately 15 g of sample into a prerinsed disposable aluminum dish. Record the weight to the nearest 0.01 g.

7.2.5 Mix the sample with Hydromatrix®, or equivalent, using approximately a 1:1 ratio by volume, until free-flowing. Depending on the matrix, the amount of sample may need to be reduced.

7.2.6 Place the extraction cell funnel on open end of cell body. Load sample into cell through funnel. Gently tap cell on hard surface to pack sample evenly, and to reduce void volume.

7.2.7 All samples should come within 1 cm of the top of the vessel. If a sample does not, use sand to fill.

7.2.8 When the transfer is complete, remove the funnel. Add 1.0 mL of 1.0 µg/mL Surrogate Standard to each sample, blank, and spike sample. Final concentration will be 0.0.067 mg/kg.

7.2.9 Add 1.0 mL of the 1.25 µg/mL Pesticide Spike Standard to samples selected for pesticide spiking. The final concentration will be 0.083 mg/kg.

7.2.10 Place filter paper on top of the sample. Either wipe cell threads with Kimwipes® or blow away any visible particles and screw the second end cap onto open end of the cell body, and tighten.

7.2.11 Place completed extraction cell into position #1 on ASE. Place the corresponding collection vial into position #1 below.

7.2.12 Repeat steps above for additional samples.

7.2.13 Fill solvent bottles with the 3:1 Hexane to Acetone Extraction Solvent Mix.

7.2.14 Make sure pressure on gas tank is set to 180 psi. Make sure that solvent bottle pressure is 10 psi, system air pressure is 50 psi, and compression oven pressure is 130 psi.

7.2.15 Refer to Equipment SOP entitled 'ASE' for equipment set-up and operation.

7.2.16 Assemble a K-D apparatus by attaching a 10 mL K-D concentrator to a 500 mL K-D flask for Nitrogen Blowdown or a 200 mL Turbo Vap II concentration vial.

7.2.17 Decant extraction solvent through a hexane rinsed funnel with sodium sulfate and glass wool. Rinse the collection vial three times with hexane to complete quantitative transfer. Collect the extract in the assembled K-D apparatus or a 200 mL Turbo Vap II concentration vial.

7.2.18 KD Technique / Nitrogen Blowdown

7.2.18.1 Add one solvent rinsed boiling bead to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of hexane to the top of the column. Place the K-D apparatus on a hot water bath (80-85 °C) so that the K-D concentrator is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot vapor. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

7.2.18.2 When the apparent volume of liquid reaches 5 mL, remove the K-D apparatus from the water bath and allow it to cool. Remove the Snyder column.

7.2.18.3 Put the K-D concentrator in a warm bath (about 35 °C) and evaporate the solvent volume to less than 5 mL using a gentle stream of clean, dry nitrogen. During evaporation, the tube solvent level must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Do not allow extract to go dry. Using a disposable pipet, adjust the final volume to 5.0 mL with hexane and mix the extract completely.

7.2.18.4 Transfer approximately 1 mL to a 2 mL autosampler vial and put the rest in a 4 mL saver vial. Store in freezer until analysis.

7.2.19 Turbo Vap II

7.2.19.1 Place the Turbo Vap collection tube in the Turbo Vap.

7.2.19.2 Set the water bath temperature to 40 °C and the pressure to 8-11 psi.

7.2.19.3 Set the Turbo Vap to monitor by 'sensor' to achieve a final volume of approximately 4 mL.

7.2.19.4 Using a disposable pipet, adjust the final volume to 5.0 mL with hexane and mix the extract completely. Transfer approximately 1 mL to a 2 mL autosampler vial and the remaining extract to a 4 mL saver vial. Store in freezer until analysis.

7.3 Calibration

7.3.1 Prepare pesticide working standards at a minimum of five concentration levels, ranging from 0.080-0.40 µg/mL, by diluting the 10 µg/mL Pesticide Intermediate Solution with hexane. A typical calibration curve would be:

Inter. Solution (mL/25 mL)	Pest. Conc. (µg/mL)	Surr. Conc. (µg/mL)
0.20	0.080	0.080
0.25	0.10	0.10
0.50	0.20	0.20
0.75	0.30	0.30
1.0	0.40	0.40

7.3.2 Prepare toxaphene working standards at a minimum of three concentration levels, ranging from 0.20-1.0 µg/mL, by diluting the 1.0 µg/mL Toxaphene Intermediate Solution with hexane. A typical calibration curve would be:

Inter. Solution (mL/1.0 mL)	Conc. (µg/mL)
0.20	0.20
0.50	0.50
1.0	1.0

7.3.3 The average response factor should be calculated for each compound. The percent relative standard deviation (%RSD) should be < 20% for each compound. If the %RSD of any compound is < 20%, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

7.3.4 If the %RSD of any compound is > 20%, construct calibration curves of area versus concentration using a first order or linear fit. Correlation coefficients should be 0.990 or greater.

7.3.5 Calibration curve calculations are found in the QA Manual.

7.3.6 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.3.7 Use the Pesticide Second Source Standard as the continuing calibration standard – CCAL/CCVS.

7.3.8 Stock Standards should be stored in a freezer and replaced following manufacturer's expiration date or one year after opening, whichever comes first. Working standards should be stored in a freezer and replaced every 6 months, or sooner if analyses of continuing calibration standards indicate degradation or loss.

7.4 Analysis

7.4.1 GC Conditions

7.4.1.1 Columns: Rtx®-CLPesticides™, 30m x 0.32mm, 0.5 µm film (Restek #11139), and Rtx®-CLPesticidesII™, 30 m x 0.32 mm, 0.25 µm film (Restek #11324) or equivalent

7.4.1.2 Injector Temperature: 250 °C

7.4.1.3 Detector Temperature: 310 °C

7.4.1.4 ECD 1 Temp Program: 150 °C for 0.5 min, 10 °C/min ramp to 200 °C, 5.0 °C/min ramp to 310 °C

7.4.1.5 ECD 2 Temp Program: 175 °C for 0 min, 6 °C/min ramp to 300 °C

7.4.1.6 Flow Rate: 1.6 mL/min (ECD 1), 1.0 mL/min (ECD 2); Constant Flow

7.4.1.7 Split Ratio: 40:1 (ECD 1), 60:1 (ECD 2)

7.4.1.8 GC Range: 0

7.4.1.9 Attenuation: 0

7.4.1.10 Injection Volume: 1.0 µL

7.4.2 4,4'-DDT and endrin are easily degraded in the injection port. Analyze the 4,4'-DDT and Endrin Breakdown Standard at the start of a daily run and every 12 hours thereafter.

7.4.3 Using the 'DDT Endrin Breakdown' form, calculate the breakdown of 4,4'-DDT and endrin as given below on both the front and back detectors. Include the breakdown report in the daily file.

$$4,4'\text{-}DDT\ Breakdown = \frac{(DDE\ response + DDD\ response)}{(DDE\ response + DDD\ response + DDT\ response)}(100)$$

$$Endrin\ Breakdown = \frac{(Endrin\ aldehyde\ response + Endrin\ ketone\ response)}{(Endrin\ aldehyde\ response + Endrin\ ketone\ response + Endrin\ response)}(100)$$

7.4.4 Calculated breakdown must be < 15% for both 4,4'-DDT and endrin. If not, corrective action should be taken. Corrective action may include reinjection, making a new standard, performing maintenance and/or flagging data.

7.4.5 Analyze the Pesticide Second Source Standard (CCAL/CCVS) at the start of a daily run, every 12 hours or 20 samples after that, which ever comes first, and at the end of a sequence. Recoveries should be ± 15% for each analyte. For MN projects, recoveries can be ± 15% for all analytes collectively. When using the collective analyte list, individual compounds that exceeded ± 15% must be flagged on the report.

7.4.6 If recoveries are not met, corrective action should be taken. Corrective action may include reinjection, making a new standard, performing maintenance and/or flagging data.

7.4.7 Typical run order

7.4.7.1 Solvent blank

7.4.7.2 DDT/Endrin breakdown

7.4.7.3 Pesticide CCVS

7.4.7.4 Samples and QC

7.4.7.5 Pesticide CCVS

7.4.8 If the response for a peak exceeds the working range of the system or the highest standard, dilute the extract with hexane and re-analyze.

7.4.9 When identification is confirmed by a second column, calculate the %RPD of the quantitative results. The %RPD should be < 40%. If it isn't, corrective action should be taken. Corrective action may include checking for overlapping peaks, examining peak integration, and/or flagging data.

7.4.10 Various sample cleanup procedures are destructive to chlorinated pesticides. A first step in cleanup should simply be allowing sediment to settle and siphon off the top solvent layer. See 8081A for specific cleanup procedures and their advantages and disadvantages.

7.5 Calculation

7.5.1 Calculate the concentration of the analyte in the sample using one of the following equations:

$$\text{Water Concentration } (\mu g / L) = \frac{(C_{ex})(V_{ex})(F)}{V_o}$$

$$\text{Soil Concentration } (mg / kg) = \frac{(C_{ex})(V_{ex})(F)}{(W)(D)}$$

C_{ex} = extract concentration, µg/mL
V_{ex} = extract volume, mL
F = dilution factor (diluted volume/extract volume)
V_o = volume of sample extracted, L
W = sample weight, g
D = % dry weight of sample/100, or 1 for wet weight basis

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

8.2 Highly contaminated samples are returned to the client for disposal.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, when there is a change in the test method that may affect how the test is performed or when there is a major change in instrumentation. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. The method blank must be less than the reporting limit or the sample batch is re-extracted if possible. If it is not possible to re-extract, the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Accuracy control limits are set at 70.0-130% for LCS and MS. Surrogate limits are generated semi-annually, using 20 Percent Recovery points, as follows:

9.3.1.1 Upper and Lower Control Limit = Mean ± 3s

9.3.1.2 Upper and Lower Warning Limit = Mean ± 2s

9.3.1.3 s = Standard deviation

9.3.1.4 For Arizona compliance, the surrogate lower control limit can not calculate below the lowest standard on the calibration curve (e.g. lowest standard = 0.08 µg/mL, spike is at 0.2 µg/mL, % can not be below 40.0%). The Minnesota Pollution Control Agency sets a guideline that the lower control limit can not be < 30.0%. For consistency between methods 608, 8081A, and 8082, LEGEND will use the greater of these which is 40.0% (8081A limit).

9.3.2 Precision control limits are set at 20.0% RPD for LCS/LCSD and generated for MS/MSD. In-house control charts are generated semi-annually, using 20 RPD points, as follows:

9.3.2.1 Control Limit = Mean + 3s

9.3.2.2 Warning Limit = Mean + 2s

9.3.2.3 s = Standard deviation

9.3.2.4 RPD = Relative Percent Difference

9.3.3 QC calculations are found in the QA Manual

9.3.4 LCS, MS and surrogates are reviewed.

9.3.5 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is re-extracted and/or re-analyzed if possible. If the batch cannot be re-analyzed, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.6 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS is flagged and/or a case narrative is written.

9.3.7 If a sample surrogate is outside the limits, the sample is re-extracted and/or reanalyzed if possible. If the sample cannot be reanalyzed, the data is flagged next to the actual result in the report.

10. REPORTING

10.1 Soil samples results are reported in mg/kg on a dry weight basis.

10.2 Toxaphene results for soil and water samples will only be calculated using data from the front column only.

10.3 Water sample results are reported in µg/L.

10.4 The reported result is rounded to two significant figures.

10.5 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

12. REFERENCES

12.1 EPA Methods 3510C, 3545, 8081A, 8000B (MN), 8000C (AZ)

Appendix A

Initial Demonstration of Capability (IDC)
Organochlorinated Pesticides in Soil and Water Samples

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards in Ottawa sand and/or lab-grade water and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual results are entered. The mean recovery in concentration and %, and the %RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: 70.0-130%
   Precision: ≤ 20.0%

   If the standards were not extracted, the results must meet the following criteria:

   Accuracy: 85.0-115%
   Precision: ≤ 20% RPD

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
Organochlorine Pesticides – Method 8081A

Parameter	Water MDL (µg/L)	Water RL (µg/L)	Soil MDL (mg/kg)	Soil RL (mg/kg)
α-BHC	0.040	0.40	0.0015	0.040
α-Chlordane	0.039	0.40	0.0014	0.040
Aldrin	0.038	0.40	0.0014	0.040
β-BHC	0.053	0.40	0.0015	0.040
δ-BHC	0.046	0.40	0.0015	0.040
Dieldrin	0.038	0.40	0.0014	0.040
Endosulfan I	0.042	0.40	0.0014	0.040
Endosulfan II	0.034	0.40	0.0015	0.040
Endosulfan sulfate	0.038	0.40	0.0016	0.040
Endrin	0.036	0.40	0.0014	0.040
Endrin aldehyde	0.042	0.40	0.0016	0.040
Endrin ketone	0.035	0.40	0.0014	0.040
γ-BHC (Lindane)	0.039	0.40	0.0015	0.040
γ-Chlordane	0.036	0.40	0.0014	0.040
Heptachlor	0.040	0.40	0.0015	0.040
Heptachlor epoxide	0.040	0.40	0.0014	0.040
Methoxychlor	0.037	0.40	0.0017	0.040
4,4'-DDD	0.036	0.40	0.0013	0.040
4,4'-DDE	0.038	0.40	0.0013	0.040
4,4'-DDT	0.034	0.40	0.0013	0.040
Toxaphene	0.15	1.0	0.012	0.080

DOCUMENT REVIEW

DOCUMENT:	LABENV-025.6
REVIEWER:	Erin Hilton / Kelly Clements
DATE:	02/21/08 03/21/08 03/28/08

SECTION	CHANGES
3.2	Added section
6.2, 7.4.1.1	Added catalog numbers
SOP	Replaced “concentrator” with “flask”
SOP	Replaced “ampule” with “K-D concentrator”
6.36	Added “(used in Pesticide Second Source Standard Solution)”
6.45	Added “1-2 drops of” and “approximately 50 mL of”
6.46	Added “CCAL/”, “Second Source” and “Store in a freezer for up to six months.”
7.14	Changed final concentration to 1.0 µg/L
7.15	Changed concentration to 1.25 µg/mL and final concentration to 1.25 µg/L
7.1.8	Added “Cap and shake vigorously for 10 seconds, and then vent.”; deleted “venting frequently” and “for a minimum of ten minutes.”
7.1.8.1	Replaced “brake” with “break”
7.1.8.2	Deleted “sodium sulfate”
7.1.14.1	Deleted “approximately”
7.1.14.2, 7.2.18.2	Deleted “and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane.”
SOP	Replaced “1 dram” with “4 mL”
7.2.2	Specified 2 filters and deleted “Repeat with one additional filter paper, so that there are two filters at the bottom of the cell.”
7.2.3	Added section
7.2.8	Changed final concentration to 0.067 mg/kg
7.2.9	Changed concentration to 1.25 µg/mL and final concentration to 0.083 mg/kg
7.2.17	Added “with hexane”
7.3.7	Added section
7.3.8	Added “Stock Standards should be stored in a freezer and replaced following manufacturer’s expiration date or one year after opening, whichever comes first.”
7.4.3	Added “DDT Endrin”; deleted “Calculation”
7.4.5	Deleted “a mid-level standard (CCVS)”; added “the Pesticide Second Source Standard (CCAL/CCVS)”, “or 20 samples after that, which ever comes first”, “. For MN projects, recoveries can be”
Appendix B	Updated MDLs

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF SEMI-VOLATILE ORGANIC COMPOUNDS IN WATER BY GC/MS

SOP NO.: LABENV-022.10

Original Information		
Prepared by:	Sandy McDonald	Date: 03/13/96
Technical Review:		Date:
QA/QC Coordinator:	Sharon Cenis	Date: 03/25/96
Authorized by:	Cheryl Sykora	Date: 03/29/96

Revision Information		
Supersedes:	LABENV-022.9	Date: 04/04/08
Revised by:	Van Pham	Date: 03/27/09
Signature:	______________________	Date: __________
Technical Review:	Triet Le	Date: 03/27/09
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 04/27/09
Signature:	______________________	Date: __________

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Supersedes:	LABENV-022.9	Date: 04/04/08
Revised by:	Van Pham	Date:
Signature:	[signature]	Date: 3/27/09
Technical Review:	Triet Le	Date:
Signature:	[signature]	Date: 3/27/09
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 4/27/09

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SOP TITLE: DETERMINATION OF SEMI-VOLATILE ORGANIC COMPOUNDS IN WATER BY GC/MS

1. PURPOSE

1.1 This document defines the preparation and analysis for semi-volatile compounds in water by Gas Chromatography/Mass Spectrometry (GC/MS). This procedure can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. The SOP is applicable to samples typically analyzed by EPA 8270C.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the SOP.

2.3 An analyst experienced in the use of gas chromatograph/mass spectrometers, skilled in the interpretation of mass spectra, and trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This method is applicable to surface water and groundwater.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized.

4.3 Follow standard laboratory safety procedures.

4.4 A lab coat and safety glasses should be worn during sample and standard preparation.

4.5 When working with organic compounds, wear chemical resistant gloves.

4.6 Prepare stock and standard solutions in a hood.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample’s integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Samples should be collected in 1L amber bottles with Teflon lined caps and stored at 4 ± 2 °C.

5.4 The recommended holding time is 7 days until extraction and analysis within 40 days of extraction.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 HP 5890 Series II Gas Chromatograph (GC) with data processing equipment, or equivalent

6.2 HP 5972A Mass Selective Detector (MSD) with scan range of 35 to 500 amu using 70 volts electron energy in the electron impact ionization mode, or equivalent

6.3 Column – 30m x 0.25 mm ID (or 0.32 mm ID) x 0.25 µm film thickness silicone-coated fused silica capillary column (DB-5MS or equivalent)

6.4 Nitrogen evaporator – N-EVAP, or equivalent

6.5 Microliter syringes – 10, 25, 100, 250, 500, and 1000 µL

6.6 Volumetric flask – 5, 10, 25, and 50 mL

6.7 Serum Bottles – amber glass with Teflon-lined crimp tops

6.8 Two liter Teflon separatory funnel

6.9 Glass funnel with Pyrex glass wool at bottom

6.10 Kuderna-Danish (K-D) concentrator – 10 mL, graduated

6.11 Kuderna-Danish (K-D) flask – 500 mL

6.12 Snyder Column – three ball macro

6.13 PTFE solvent rinsed boiling beads, or equivalent

6.14 Water bath

6.15 Autosampler vials – 2 mL amber glass with Teflon lined crimp tops

6.16 pH paper (0-14 Std. Units)

6.17 Graduated cylinder – 1 liter

6.18 Graduated disposable pipets – 1 or 2 mL

6.19 Organic free water

6.20 Sodium Hydroxide (NaOH) – reagent grade

6.21 10N Sodium Hydroxide – dissolve 40 g of the NaOH in 100 mL organic free water

6.22 Sulfuric Acid (H_2SO_4) – reagent grade

6.23 1:1 Sulfuric Acid – slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of organic free water

6.24 Anhydrous Sodium Sulfate (Na_2SO_4) – muffle at 400 °C for four hours before using

6.25 Methylene Chloride (CH_2Cl_2) – pesticide grade, or equivalent

6.26 Acetone – pesticide grade, or equivalent

6.27 Methanol – pesticide grade, or equivalent

6.28 GC/MS Tune Check Stock – 500 µg/mL each of DFTPP, Benzidine, 4.4'-DDT, and pentachlorophenol, Absolute Standards, Inc. #43030, or equivalent

6.29 Calibration Stock 1 – 2000 µg/mL each of bis(2-chloroethoxy) methane, bis(2-chloroethyl) ether, bis(2-ethylhexyl) phthalate, bis(2-chloroisopropyl)ether, 4-bromophenyl phenyl ether, butyl benzyl phthalate, 4-chlorophenyl phenyl ether, diethyl phthalate, dimethyl phthalate, di-n-butyl phthalate, di-n-octyl phthalate, n-nitrosodimethylamine, n-nitrosodi-n-propylamine, and n-nitrosodiphenylamine, Absolute #10001, or equivalent

6.30 Calibration Stock 2 – 2000 µg/mL each of acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, carbazole, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene Absolute #10007, or equivalent

6.31 Calibration Stock 3 – 2000 µg/mL each of azobenzene (1,2-diphenylhydrazine), 2-chloronaphthalene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, 1,3 dichlorobenzene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclopentadiene, hexachloroethane, isophorone, nitrobenzene, and 1,2,4-trichlorobenzene, Absolute #10002, or equivalent

6.32 Calibration Stock 4 – 2,000 µg/mL each of aniline, benzyl alcohol, 4-chloroaniline, dibenzofuran, 2-methylnaphthalene, 2-nitroaniline, 3-nitroaniline, and 4-nitroaniline, Absolute #10005, or equivalent

6.33 Calibration Stock 5 – 2,000 µg/mL each of benzoic acid, 2-methylphenol, 4-methylphenol, and 2,4,5-trichlorophenol, Absolute #10004, or equivalent

6.34 Calibration Stock 6 – 2,000 µg/mL each of 4-chloro-3-methylphenol, 2-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4-dimethylphenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 2-nitrophenol, 4-nitrophenol, pentachlorophenol, phenol, 2,4,6-trichlorophenol, and 2,3,4,6-tetrachlorophenol, Absolute #10018, or equivalent

6.35 Calibration Stock 7 – 2,000 µg/mL each of benzidine and 3,3'-dichlorobenzidine, Absolute #10006, or equivalent

6.36 Calibration Stock 8 – 1,000 µg/mL of pyridine, Absolute #70260, or equivalent

6.37 Internal Standard Stock – 4,000 µg/mL each of acenaphthene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, naphthalene-d_8, perylene-d_{12}, and phenanthrene-d_{10}, Absolute #10009, or equivalent

6.38 Calibration Surrogate Stock 1 – 10,000 µg/mL each of 2-flurophenol, phenol-d6, and 2,4,6-tribromophenol, Absolute #21015, or equivalent

6.39 Calibration Surrogate Stock 2 – 5,000 µg/mL each of nitrobenzene-d_5, 2-fluorobiphenyl, and terphenyl-$d_{14,}$ Absolute #21016, or equivalent

6.40 Sample/Second Source Surrogate Stock 1 – 10,000 µg/mL each of 2-flurophenol, phenol-d6, and 2,4,6-tribromophenol, Restek #31087, or equivalent

6.41 Sample/Second Source Surrogate Stock 2 – 5,000 µg/mL each of nitrobenzene-d_5, 2-fluorobiphenyl, and terphenyl-$d_{14,}$ Restek #31086, or equivalent

6.42 Spike Stock 1 – 10,000 µg/mL each of pentachlorophenol, phenol, 2-chlorophenol, 4-chloro-3-methylphenol, and 4-nitrophenol, Restek #31071, or equivalent

6.43 Spike Stock 2 – 5,000 µg/mL each of 1,2,4-trichlorobenzene, acenaphthene, 2,4-dinitrotoluene, pyrene, n-nitrosodi-n-propylamine, and 1,4-dichlorobenzene, Restek #31084, or equivalent

6.44 Spike Stock 3 – 2,000 µg/mL each of acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, 2-methylnaphthalene, naphthalene, phenanthrene, and pyrene, Absolute #50003, or equivalent

6.45 Second Source Stock 9 - 1000ug/ml of all 8270 components except for benzidine, 3,3'-dichlorobenzidine, 2,6-dichlorophenol, surrogates, and benzoic acid , Restek # 31850 or equivalent

6.46 Second Source Stock 10 - 2000ug/ml each of benzidine and 3,3'-dichlorobenzidine, Restek # 31834 or equivalent

6.47 Second Source Stock 11 - 1000ug/ml of 2,6-dichlorophenol, Restek # 31409 or equivalent

6.48 Second source stock 12 - 1000ug/ml of benzoic acid, Absolute #70034, or equivalent

6.49 Calibration Intermediate Solution – combine 300 µL of the 2,000 µg/mL Calibration Stocks 1-7, 600 µL of the 1,000 µg/mL Calibration Stock 8, 60 µL of the 10,000 µg/mL Surrogate Stock 1, 120 µL of the 5,000 µg/mL Surrogate Stock 2, and 120 µL of methylene chloride (3 mL final volume) to produce a 200 µg/mL Calibration Intermediate Solution

6.50 GC/MS Tune Check Standard – dilute 100 µL of the 500 µg/mL GC/MS Tune Check Stock with 900 µL of methylene chloride to produce a 50 µg/mL GC/MS Tune Check Standard

6.51 Sample Surrogate Standard – dilute 0.5 mL of the 10,000 µg/mL Surrogate Stock 1 and 1 mL of the 5,000 µg/mL Surrogate Stock 2 to a final volume of 50 mL with methanol to produce a 100 µg/mL Sample Surrogate Standard

6.52 Spike Standard – dilute 0.5 mL of the 10,000 µg/mL Spike Stock 1, 1 mL of the 5,000 µg/mL Spike Stock 2, and 2.5 mL of the 2,000 µg/mL Spike Stock 3 to a final volume of 50 mL with methanol to produce a 100 µg/mL Spike Standard

6.53 Second Source ICV - combine 50 µL of the 1,000 µg/mL Stocks 9, 11 and 12, 25 µL of the 2000 µg/mL Stock 10, 5.0 µL of the 10,000 µg/mL Sample Surrogate Stock 1, 10 µL of the 5,000 µg/mL Sample Surrogate Stock 2, and 810 µL of methylene chloride (1 mL final volume) to produce a 50 µg/mL Second Source Calibration Solution. Add 10 µL of the 4,000 µg/mL Internal Standard Stock prior to analysis to produce an ISTD concentration of 40 µg/mL.

6.54 All solutions and standards should be stored in a freezer at $\leq$ -10 ºC and should be freshly prepared each year, or sooner if check standards or continuing calibration standards indicate a problem.

7. PROCEDURE

7.1 Preparation of Water Samples

7.1.1 Pre-rinse all glassware once with acetone, once with hexane, and three times with $MeCl_2$.

7.1.2 Mark the water level on the outside of the bottle for later determination of volume.

7.1.3 Measure the pH of the sample and transfer to a pre-rinsed two-liter separatory funnel. (Note: If an evident layer of sediment is present, decant the sample and record on the extraction sheet.)

7.1.4 If analysis of acid and base/neutral compounds is required, first extract the sample three times with the pH being <2 and then three times with the pH being >11.

7.1.5 If the analysis of acid compounds ONLY is required, adjust the pH to <2 with 1:1 H_2SO_4.

7.1.6 If the analysis of base/neutral compounds ONLY is required, adjust the pH to >11 with 10N NaOH.

7.1.7 Add 50 mL of acetone to all samples, spikes, and blanks.

7.1.8 Add 1.0 mL of the 100 µg/mL Sample Surrogate Standard to all samples, spikes, and blanks. Final concentration will be 100 µg/L assuming a 1.0 mL final volume, 1 µL injection, and 1,000 mL sample volume.

7.1.9 For the samples in each analytical batch selected for spiking, add 1.0 mL of the 100 µg/mL Spike Standard. Final concentration will be 100 µg/L assuming a 1.0 mL final volume, 1 µL injection, and 1,000 mL sample volume. A typical batch will have an LCS and MS/MSD. LCS/LCSD will be substituted if enough sample is not provided.

7.1.10 Add approximately 60 mL of methylene chloride to the sample bottle and rinse. Transfer to the separatory funnel with the sample. (Note: If the sample was decanted, add the 60 mL of methylene chloride directly to the separatory funnel.)

7.1.11 Cap and shake vigorously for 10 seconds then vent. Continuously shake for an additional 2 minutes. Allow the methylene chloride to separate from the sample.

7.1.12 If an emulsion interface between layers is more than one-third the size of the solvent layer, the analyst should perform a beaker break without the use of Na_2SO_4.

7.1.12.1 Using a beaker, transfer the solvent layer to a glass 100 mm funnel containing a glass wool plug and about 2-3 inches of anhydrous muffled Na_2SO_4. Rinse the beaker with $MeCl_2$ and add to the funnel.

7.1.13 Drain into a 500 mL K-D flask equipped with a 10 mL K-D concentrator for Nitrogen Blowdown.

7.1.14 Repeat steps above with two additional fresh portions of methylene chloride.

7.1.15 After the final extraction, rinse the sodium sulfate with 20-30 mL of methylene chloride to complete the quantitative transfer.

7.1.16 If the emulsion layer is still present after the final shake, the analyst should employ mechanical techniques to complete the phase separation. Refer to the protocol found in Work Instruction (WI) ‘Handling Emulsions’

7.1.17 Fill sample bottle with tap water to mark made previously. Transfer to a 1000 mL graduated cylinder and record volume on extraction sheet.

7.1.18 K-D Technique / Nitrogen Blowdown

7.1.18.1 Add one solvent rinsed boiling bead to the flask, 10 mL of acetone, and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-85 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot vapor. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches approximately 20 mL, add 10 mL of acetone through the Snyder column.

7.1.18.2 Concentrate to approximately 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool. Remove the Snyder column.

7.1.18.3 Put the K-D concentrator in a warm bath (35 ºC) and evaporate the solvent volume to less than 1 mL using a gentle stream of clean, dry nitrogen. During evaporation, the tube solvent level must be positioned to avoid water condensation (i.e. the solvent level should be below the level of the water bath). Do not allow the extract to go dry at any point. This may result in a loss of analytes, especially the phenols.

7.1.18.4 Using a disposable graduated pipet, adjust the final volume to 1.0 mL with methylene chloride and mix the extract completely.

7.1.18.5 Transfer to a 2 mL autosampler vial. Store in freezer until analysis.

7.2 Calibration

7.2.1 Initial Calibration

7.2.1.1 The GC/MS must be tuned to meet the criteria in Table 1 for a 50 ng injection of DFTPP. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachorophenol should be present at their normal responses, and no peak tailing should be visible.

7.2.1.2 Use the base peak ion from the specific internal standard as the primary ion for quantitation, unless interferences are noted.

7.2.1.3 Prepare working standards at a minimum of 5 concentration levels, ranging from 5.0-150 µg/mL (except benzo(k)fluoranthene and benzo(g,h,i)perylene range from 5.0-100 µg/mL, and pentachlorophenol ranges from 10-150 µg/mL), by diluting the 200 µg/mL Calibration Intermediate Solution with methylene chloride. A typical calibration curve would be:

Calib. Inter. Solution (µL/1 mL)	Concentration (µg/mL)
25	5.0
50	10
100	20
250	50
400	80
500	100
750	150

7.2.1.4 Add 10 µL of the 4,000 µg/mL Internal Standard Stock to each calibration standard prior to analysis to produce an ISTD concentration of 40 µg/mL.

7.2.1.5 Calculate response factors (RFs) for each compound at each level relative to the preceding internal standard (see Table 2).

7.2.1.6 The average response factor should be calculated for each compound. The percent relative standard deviation (%RSD) should be less than 15% for each compound. However, the %RSD for each Calibration Check Compound (CCC), (see Table 3), must be less than 30%. If these criteria cannot be met, corrective action must be taken and the system recalibrated. Possible problems include standard mixture degradation, injection port inlet contamination, contamination of the front end of the column, or active sites in the column or chromatographic system.

7.2.1.7 System Performance Check Compounds (SPCC) must meet minimum average response factor criteria (see Table 4). For examples of corrective action, see above.

7.2.1.8 If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation. A minimum of five calibration points may be used to define the working range.

7.2.1.9 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/A_{is}) versus concentration using first order regression fit. Second order (quadratic) curves may be constructed for some compounds that respond poorly in the chromatographic system (e.g. benzyl alcohol, benzoic acid, benzidine, phenol, 4-nitrophenol, 2,3,4,6-tetrachlorophenol, 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol, 2,4,6-tribromophenol, pentachlorophenol, hexachlorocyclopentadiene, acenaphthylene, diethyl phthalate, naphthalene, 2-methylnaphthalene, 2-chloronaphthalene, fluorene, benzo[b] & [k]fluoranthene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, fluorene, and benzo[b] & [k]fluoranthene). Second order fit may not be used in place of instrument maintenance. A correlation coefficient of 0.99 or better is required for each curve fit.

7.2.1.10 Immediately after an initial calibration curve is generated it must be verified by a second source verification standard. Acceptance criteria will be set at 70.0 – 130%.

7.2.1.11 Calibration curve calculations are found in the QA Manual.

7.2.1.12 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% (± 50% for AZ samples) or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.2.2 Daily GC/MS calibration

7.2.2.1 The GC/MS tuning standard containing 50 ng of DFTPP must meet the Table 1 criteria. This standard must be run and meet these criteria every 12 hours.

7.2.2.2 A mid-level calibration standard must be analyzed every 12 hours. The SPCCs must meet the minimum response criteria on Table 4.

7.2.2.3 Use the Calibration Check Compounds (CCCs), found in Table 3, to check the validity of the initial calibration. Calculate the percent drift using:

$$\%Drift = \frac{(C_I - C_c)}{(C_I)}(100)$$

C_I = Calibration Check Compound standard concentration
C_c = Measured concentration using selected quantitation method

If the percent difference for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. Non-CCC must meet the acceptance criteria of $\leq$ 20% for Arizona compliance samples.

7.2.2.4 Evaluate the internal standard responses and retention times. If the retention time changes by more than 30 seconds from the mid-point of the last initial calibration curve or the Extracted Ion Current Profile (EICP) area for any internal standard changes by a factor of two (- 50% to + 100%) from the mid-point of the last initial calibration curve, the chromatographic system must be inspected for malfunctions and corrections made as required before samples can be analyzed.

7.2.2.5 If any of the daily calibration criteria are not met, minor corrective maintenance may be performed on the system and the calibration check standard re-run. If major corrective action was required, such as cleaning the source or replacing the chromatographic column, a new initial calibration would need to be generated before samples could be analyzed.

7.3 Analysis

7.3.1 GC/MS Conditions

7.3.1.1 Mass Range: 35-500 amu

7.3.1.2 Scan Time: 1 scan/sec

7.3.1.3 Initial Temperature: 40 °C, hold for 4 minutes

7.3.1.4 Temp. Program: 40- 320 °C at 10 °C/min

7.3.1.5 Final Temperature: 320 °C, hold until at least 1 minute after benzo(g,h,i)perylene has eluted

7.3.1.6 Injector Temperature: 250-300 °C

7.3.1.7 Interface Temperature: 250-300 °C

7.3.1.8 Injector: Split/Splitless

7.3.1.9 Sample volume: 1 µL

7.3.1.10 Carrier gas: Helium at 1 mL/min

7.3.2 Add 10 µL of the 4,000 µg/mL Internal Standard Stock to each sample extract to produce an ISTD concentration of 40 µg/mL.

7.3.3 Inject 1 µL of the 1 mL sample extract. If the response for any quantitation ion exceeds the initial calibration curve, make an appropriate dilution, add additional internal standard as required to maintain 40 µg/mL of each internal standard. Reanalyze the diluted extract.

7.3.4 Recap sample vials prior to storing in freezer.

7.4 Calculation

7.4.1 Qualitative analysis

7.4.1.1 The retention time of the sample compound must fall within ± 30 seconds of the retention time of the standard compound run within the last 12 hours.

7.4.1.2 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. Use a mid-level initial calibration standard to obtain standard reference spectra.

7.4.1.3 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. The relative intensities of the ions should agree within ± 30% between the sample and reference spectrum.

7.4.1.4 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification.

7.4.2 Quantitative analysis

7.4.2.1 Quantitate using the internal standard technique. Use the internal standard preceding the analyte (see Table 2). Quantitation is based on the integrated abundance from the EICP of the primary characteristic ion.

7.4.2.2 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data and the following equation:

$$Concentration\left(\mu g / L\right) = \frac{(A_x)(C_{is})(F)(V_{ex})}{(A_{is})(RF)(V_s)}$$

A_x = Area of characteristic ion being measured
C_{is} = Amount of internal standard injected (µg/mL)
F = Dilution factor
V_{ex} = Volume of extract, mL
A_{is} = Area of characteristic ion for the internal standard
RF = Mean response factor for compound being measured
V_s = Volume of sample, L

7.4.2.3 Alternatively, the regression line fitted to the initial calibration may be used for the determination of the analyte concentration.

7.4.2.4 Where applicable, an estimate of concentration for noncalibrated components (Tentatively Identified Compounds – TIC) in the sample can be made. The concentration should be reported as an estimate assuming a response factor of 1 using the nearest internal standard.

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

8.2 Highly contaminated samples are returned to the client for disposal.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, when there is a change in the test method that may affect how the test is performed or when there is a major change in instrumentation. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. The method blank must be less than the reporting limit or the sample batch is re-extracted if possible. If it is not possible to re-extract, the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Accuracy control limits are generated for LCS, MS and surrogates. In-house control charts are generated semi-annually, using 20 Percent Recovery points, as follows:

9.3.1.1 Upper and Lower Control Limit = Mean ± 3s

9.3.1.2 Upper and Lower Warning Limit = Mean ± 2s

9.3.1.3 s = Standard deviation

9.3.1.4 For Arizona compliance, the lower control limit cannot calculate below the lowest standard on the calibration curve (e.g. lowest standard = 5.0 µg/mL, spike is at 100 µg/mL, % can not be below 5.0%). The Minnesota Pollution Control Agency sets a guideline that the lower control limit can not be < 30.0%. LEGEND will use the greater of these two; 30.0% in this example.

9.3.2 Precision control limits are set at 20.0% RPD for LCS/LCSD and generated for MS/MSD. In-house control charts are generated semi-annually, using 20 RPD points, as follows:

9.3.2.1 Control Limit = Mean + 3s

9.3.2.2 Warning Limit = Mean + 2s

9.3.2.3 s = Standard deviation

9.3.2.4 RPD = Relative Percent Difference

9.3.3 QC calculations are found in the QA Manual.

9.3.4 LCS, MS and surrogates are reviewed.

9.3.5 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is re-extracted and/or re-analyzed if possible. If the batch cannot be re-extracted and/or re-analyzed, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.6 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS is flagged and/or a case narrative is written.

9.3.7 If a sample surrogate is outside the limits, the sample is re-extracted and/or reanalyzed if possible. If the sample cannot be re-extracted and/or reanalyzed, the data is flagged next to the actual result in the report.

10. REPORTING

10.1 Sample results are reported in µg/L.

10.2 The reported result is rounded to two significant figures.

10.3 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Report Limits

12. REFERENCES

12.1 EPA Methods 3500B, 3510C, 8270C, 8000B (MN), 8000C (AZ)

12.2 Vendor equipment manuals

TABLE 1 – DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	10-80% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	10-80% of mass 198
197	< 2% of mass 198
198	Base peak or >50% of 442
199	5-9% of mass 198
275	10-60% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	Base peak or > 50% of mass 198
443	15-24% of mass 442

TABLE 2 – Semi-Volatile Compounds

Parameter	Primary Ion
1,4-Dichlorobenzene-d_4(IS)	152
n-Nitrosodimethylamine	74
2-Fluorophenol (surr.)	112
Aniline	93
bis(2-Chloroethyl)ether	93
Phenol-d_6 (surr.)	99
Phenol	94
2-Chlorophenol	128
1,3-Dichlorobenzene	146
1,4-Dichlorobenzene	146
1,2-Dichlorobenzene	146
Benzyl alcohol	108
bis(2-Chloroisopropyl)ether	45
2-Methylphenol	108
Hexachloroethane	117
N-Nitrosodi-n-propylamine	70
4-Methylphenol	108
Naphthalene-d_8 (IS)	136
Nitrobenzene-d_5 (surr.)	82

TABLE 2 – Semi-Volatile Compounds (continued)

Parameter	Primary Ion
Nitrobenzene	77
Isophorone	82
2-Nitrophenol	139
2,4-Dimethylphenol	107
Bis(2-Chloroethoxy)methane	93
2,4-Dichlorophenol	162
1,2,4-Trichlorobenzene	180
Naphthalene	128
Benzoic acid	122
2,6-Dichlorophenol	162
4-Chloroaniline	127
Hexachlorobutadiene	225
4-Chloro-3-methylphenol	107
2-Methylnaphthalene	142
Acenaphthene-d_{10} (IS)	164
Hexachlorocyclopentadiene	237
2,4,6-Trichlorophenol	196
2,4,5-Trichlorophenol	196
2-Fluorobiphenyl (surr.)	172
2-Chloronaphthalene	162
2-Nitroaniline	65
Acenaphthylene	152
Dimethylphthalate	163
2,6-Dinitrotoluene	165
Acenaphthene	153
3-Nitroaniline	138
2,4-Dinitrophenol	184
Dibenzofuran	168
2,4-Dinitrotoluene	165
4-Nitrophenol	109
2,3,4,6-Tetrachlorophenol	232
Fluorene	166
4-Chlorophenyl-phenylether	204
Diethylphthalate	149
4-Nitroaniline	138

TABLE 2 – Semi-Volatile Compounds (continued)

Parameter	Primary Ion
Phenanthrene-d_{10} (IS)	188
4,6-Dinitro-2-methylphenol	198
N-Nitrosodiphenylamine	169
Azobenzene	77
2,4,6-Tribromophenol (surr.)	330
4-Bromophenyl-phenylether	248
Hexachlorobenzene	284
Pentachlorophenol	266
Phenanthrene	178
Anthracene	178
Carbazole	167
Di-n-butylphthalate	149
Fluoranthene	202
Chrysene-d_{12} (IS)	240
Benzidine	184
Pyrene	202
Terphenyl-d_{14} (surr.)	244
Butylbenzylphthalate	149
3,3'-Dichlorobenzidine	252
Benzo(a)anthracene	228
Chrysene	228
bis(2-Ethylhexyl)phthalate	149
Perylene-d_{12} (IS)	264
Di-n-octylphthalate	149
Benzo(b)fluoranthene	252
Benzo(k)fluoranthene	252
Benzo(a)pyrene	252
Indeno(1,2,3-cd)pyrene	276
Dibenz(a,h)anthracene	278
Benzo(g,h,i)perylene	276

TABLE 3 – Calibration Check Compounds (CCC)

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE 4 – System Performance Check Compounds (SPCC)

Compounds	Minimum Response Factor
N-Nitroso-di-n-propylamine	0.050
Hexachlorocyclopentadiene	0.050
2,4-Dinitrophenol	0.050
4-Nitrophenol	0.050

Appendix A

Initial Demonstration of Capability (IDC)
Semi-volatile Organic Compounds (SVOC)

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards in lab-grade water and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: LCS limits
   Precision: LCS limits

   If the standards were not extracted, the results must meet the following criteria:

   Accuracy: 80.0-120%
   Precision: ≤ 20% RPD

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
Semi-Volatile Organic Compounds (SVOC)

Parameter	MDL (µg/L)	RL (µg/L)	Parameter	MDL (µg/L)	RL (µg/L)
1,2,4-Trichlorobenzene	0.15	10	Benzo(b)fluoranthene	0.22	10
1,2-Dichlorobenzene	0.23	10	Benzo(k)fluoranthene	0.31	10
1,3-Dichlorobenzene	0.21	10	Benzo(g,h,i)perylene	0.26	10
1,4-Dichlorobenzene	0.22	10	Benzoic Acid	0.52	10
2,3,4,6-Tetrachlorophenol	0.59	10	Benzyl Alcohol	0.48	10
2,4,5-Trichlorophenol	0.46	10	bis(2-Chloroethoxy)methane	0.18	10
2,4,6-Trichlorophenol	0.31	10	bis(2-Chloroethyl)ether	0.11	10
2,4-Dichlorophenol	0.24	10	bis(2-Chloroisopropyl)ether	0.065	10
2,4-Dimethylphenol	1.6	10	bis(2-Ethylhexyl)phthalate	0.24	10
2,4-Dinitrophenol	1.0	10	Butylbenzylphthalate	0.12	10
2,4-Dinitrotoluene	0.22	10	Carbazole	0.23	10
2,6-Dichlorophenol	0.20	10	Chrysene	0.22	10
2,6-Dinitrotoluene	0.25	10	Dibenz(a,h)anthracene	0.23	10
2-Chloronaphthalene	0.28	10	Dibenzofuran	0.39	10
2-Chlorophenol	0.45	10	Diethylphthalate	0.22	10
2-Methylnaphthalene	0.66	10	Dimethylphthalate	0.24	10
2-Methylphenol	0.63	10	Di-n-butylphthalate	0.22	10
2-Nitroaniline	0.35	10	Di-n-octylphthalate	0.23	10
2-Nitrophenol	0.44	10	Fluoranthene	0.39	10
3,3'-Dichlorobenzidine	7.1	25	Fluorene	0.40	10
3-Nitroaniline	1.2	10	Hexachlorobenzene	0.20	10
4,6-Dinitro-2-methylphenol	0.65	10	Hexachlorobutadiene	0.26	10
4-Bromophenyl-phenylether	0.13	10	Hexachlorocyclopentadiene	0.31	10
4-Chloro-3-methyl phenol	0.40	10	Hexachloroethane	0.31	10
4-Chloroaniline	2.3	10	Indeno(1,2,3-cd)pyrene	0.31	10
4-Chlorophenyl-phenylether	0.25	10	Isophorone	0.16	10
4-Methylphenol	0.79	10	Naphthalene	0.37	10
4-Nitroaniline	0.59	10	Nitrobenzene	0.39	10
4-Nitrophenol	1.2	10	n-Nitrosodimethylamine	0.95	10
Acenaphthene	0.36	10	n-Nitrosodi-n-propylamine	0.18	10
Acenaphthylene	0.25	10	n-Nitrosodiphenylamine	0.23	10
Aniline	2.2	10	Pentachlorophenol	0.43	10
Anthracene	0.37	10	Phenanthrene	0.39	10
Azobenzene (1,2-Diphenylhydrazine)	0.23	10	Phenol	0.55	10
Benzidine	13	100	Pyrene	0.22	10
Benzo(a)anthracene	0.37	10	Pyridine	1.9	10
Benzo(a)pyrene	0.29	10	---	---	---

DOCUMENT REVIEW

DOCUMENT:	SOP LABENV-022.10
REVIEWER:	Van Pham
DATE:	02/11/09

SECTION	CHANGE	RATIONALE
6.40 & 6.41	Added 'Second Source'	Added second source standard
6.45 → 6.48, 6.53	Added second source standards	Second source standard required
7.2.1.9	Added 'naphthalene, 2-methylnaphthalene, 2-chloronaphthalene, fluorene, benzo[b] & [k]fluoranthene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene,'	Identified as poorly responding compounds
7.2.1.10	Inserted subsection	Consistent with soil procedure
Appendix B	Updated MDLs	Annual update

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY / MASS SPECTROMETRY (GC/MS)

SOP NO.: LABENV-020.6

Original Information		
Prepared by:	Sandy McDonald	Date: 03/18/96
Technical Review:	Sharon Cenis	Date: 03/28/96
QA/QC Coordinator:		Date:
Authorized by:	Cheryl Sykora	Date: 04/03/96

Revision Information		
Supersedes:	LABENV-020.5	Date: 03/31/08
Revised by:	Henrik Pham	Date: 05/18/09
Signature:	____________________	Date: __________
Technical Review:	Sonny Hang	Date: 05/18/09
Signature:	____________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 05/18/09
Signature:	____________________	Date: __________

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Revision Information		
Supersedes:	LABENV-020.5	Date: 03/31/08
Revised by:	Henrik Pham	Date:
Signature:	[signature]	Date: 5/18/09
Technical Review:	Sonny Hang	Date:
Signature:	[signature]	Date: 5/18/09
Authorized by:	Cheryl Sykora	Date:
Signature:	[signature]	Date: 5/18/09

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FORM GEN-021 (05/07)

SOP TITLE: DETERMINATION OF VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS)

1. PURPOSE

1.1 This document defines the preparation and analysis for volatile organic compounds (VOCs) using purge and trap techniques. This document also describes the calibration and analysis of these compounds using a gas chromatograph coupled with a mass selective detector. The SOP is applicable to samples typically analyzed by EPA 8260B.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the SOP.

2.3 An analyst experienced in the use of gas chromatograph/mass spectrometers, skilled in the interpretation of mass spectra, and trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 The method is applicable to water, soil, and hazardous waste.

3.2 Interferences

3.2.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap.

3.2.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

3.2.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum of the sample container into the samples during shipment and storage. A trip blank prepared from organic-free water and carried through the sampling, handling and storage protocols can serve as a check for such contamination.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 The toxicity or carcinogenicity of most chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized.

4.3 Benzene has been classified as a known or suspected human or mammalian carcinogen. Pure standard materials and stock solutions of benzene should be handled in a hood.

4.4 Follow standard laboratory safety procedures.

4.5 A lab coat and safety glasses should be worn when preparing standards and samples.

4.6 When working with organic compounds, wear analyte resistant gloves.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Water samples should be collected in a minimum of three 40 mL VOA vials preserved with HCl to pH < 2 with no headspace and stored at 4 ± 2 °C.

5.4 The recommended holding time for preserved water samples is 14 days. If the sample is not preserved to pH < 2, the holding time is 7 days.

5.5 Soil samples should be collected in 40 mL weighed jars preserved with methanol and stored at 4 ± 2 °C.

5.6 The recommended holding time for soil samples is 14 days.

5.7 Be sure no solid material interferes with the sealing of sample containers and maintain hermetic seal on all sample containers until time of analysis.

5.8 Refrigerate samples upon receipt.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 HP 5890 Series II Gas Chromatograph (GC) with data processing equipment, or equivalent

6.2 Thermo Electron Corporation Focus GC with data processing equipment, or equivalent

6.3 HP 5972 Mass Selective Detector (MSD) with scan range of 35 to 300 amu using 70 volts electron energy in the electron impact ionization mode, or equivalent

6.4 Thermo Electron Corporation DSQ II (MSD) with scan range of 35 to 300 amu using 70 volts electron energy impact ionization mode, or equivalent

6.5 Column – 25 m x 0.20 mm ID 1.1 µm film thickness silicone-coated fused silica capillary column (DB-624 or equivalent)

6.6 Encon sample concentrator connected to an Archon autosampler, or equivalent

6.7 O.I Analytical Eclipse sample concentrator 4660 connected to O.I Analytical auto sampler 4552

6.8 Microliter syringes – 10, 25, 100, 250, 500, and 1000 µL

6.9 VOCARB 3000 trap for Encon sample concentrator, Supelco purging trap #10 for O.I Analytical Eclipse sample concentrator

6.10 Conical vials – 1 mL with mininert valves.

6.11 VOA vials with Teflon lined septa - 20 and 40 mL

6.12 Top loading balance, capable of reading to 0.01 g

6.13 Stainless steel spatula

6.14 Organic free water – purchased from Glenwood Inglewood, or equivalent

NOTE: The water is to be used for standard preparation, method blanks, dilutions, trip and field blanks.

6.15 Methanol – purge and trap grade

6.16 Calibration Stock 1 – 200 µg/mL each of bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, dichlorofluoromethane, trichlorofluoromethane and vinyl chloride, Absolute Standards, Inc. #60011, or equivalent

6.17 Calibration Stock 2 – 2,000 µg/mL of ETBE, Absolute Standards, Inc. #92450, or equivalent

6.18 Calibration Stock 3 – 200 µg/mL each of the compounds listed in Appendix B except for those listed above in Calibration Stocks 1-3, Absolute Standards, Inc. #61005, or equivalent

6.19 Spike Stock 1 – 200 µg/mL each of bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, dichlorofluoromethane, trichlorofluoromethane and vinyl chloride, Absolute Standards, Inc. #60011, or equivalent (must be a different lot number than Calibration Stock 1)

6.20 Spike Stock 2 – 200 µg/mL each of the compounds listed in Appendix B except for those listed above in Calibration Stocks 1-3, Absolute Standards, Inc. #61005, or equivalent (must be a different lot number than Calibration Stock 4)

6.21 GC/MS Tune Check/Surrogate Stock – 2,500 µg/mL each of 4-bromofluorobenzene (BFB), dibromofluoromethane, and toluene-d8, Restek #30073, or equivalent

6.22 Internal Standard Stock – 2,000 µg/mL each of 1,4-difluorobenzene, 2-bromo-1-chloropropane, 1,4-dichlorobenzene-d4, and pentafluorobenzene, Absolute Standards, Inc. #21013, or equivalent

6.23 Calibration Intermediate Solution 1 – dilute 250 µL of the 200 µg/mL Calibration Stock 1, 250 µL of the 200 µg/mL Calibration Stock 3, and 20 µL of the 2,500 µg/mL GC/MS Tune Check/Surrogate Stock to 1 mL with methanol to produce a 50 µg/mL Calibration Intermediate Solution 1

6.24 Calibration Intermediate Solution 2 (ETBE) – dilute 25 µL of the 2,000 µg/mL Calibration Stock 2 to 1mL with methanol to produce a 50 µg/mL Calibration Intermediate Solution 2

6.25 Calibration Intermediate Solution 3 – dilute 100 µL of the 50 µg/mL Calibration Intermediate Standard 1 to 1 mL with methanol to produce a 5.0 µg/mL Calibration Intermediate Solution 3

6.26 GC/MS Tune Check Standard – dilute 20 µL of the 2,500 µg/mL GC/MS Tune Check/Surrogate Stock and 25 µL of the 2,000 µg/mL Internal Standard Stock to 1 mL with methanol to produce a 50 µg/mL GC/MS Tune Check Standard

NOTE: This standard may also be used as a surrogate/internal standard for samples not loaded by the auto samplers but directly loaded by the analyst onto the sample concentrators

6.27 Auto sampler Internal Standard Solution – dilute 625 µL of the 2,000 µg/mL Internal Standard Stock to 5.0 mL with methanol to produce a 250 µg/mL auto sampler Internal Standard Solution

6.28 Auto sampler Surrogate Standard – dilute 500 µL of the 2,500 µg/mL GC/MS Tune Check/Surrogate Stock to 5.0 mL with methanol to produce a 250 µg/mL auto sampler Surrogate Standard

6.29 Spike Standard – dilute 250 µL each of the 200 µg/mL Spike Stock 1 and 2 to 1.0 mL with methanol to produce a 50 µg/mL Spike Standard

7. PROCEDURE

7.1 Preparation of Water Samples

7.1.1 Water samples are ready for analysis in the 40 mL vials.

7.2 Preparation of Soil Samples

7.2.1 Re-weigh the jar containing the soil and methanol to check sample weight.

7.2.1.1 If a 40 mL VOA vial was used and the sample weighs more than 10 g, add enough methanol to maintain a 1:1 soil to methanol ratio, if possible. Record the sample weight and the amount of methanol added. Flag data for samples containing less than 8 g or more than 20 g of soil, and those where a 1:1 ratio could not be maintained.

7.2.1.2 If a 2 oz. jar was used and the sample weighs more than 25 g, add enough methanol to maintain a 1:1 soil to methanol ratio, if possible. Record the sample weight and the amount of methanol added. Flag data for samples containing less than 20 g or more than 35 g of soil, and those where a 1:1 ratio could not be maintained.

7.2.2 Add 400 µL of methanol extract to 40 mL of organic-free water in a VOA vial.

7.3 Calibration

7.3.1 Initial Calibration

7.3.1.1 The GC/MS must be tuned to meet the criteria in Table 1 for 50 ng of BFB on column by either direct injection or by purging.

7.3.1.2 For 8260 water matrix ICAL: Prepare working standards at a minimum of five concentration levels, ranging from 1-200 µg/L, by diluting the 5.0 µg/mL Calibration Intermediate Solution 3 and the 50 µg/mL Calibration Intermediate Solution 1. A typical calibration curve would be:

Inter. Solution 3 5.0 µg/mL (µL/40 mL)	Inter. Solution 1 50 µg/mL (µL/40 mL)	Final Conc. (µg/L)
8	---	1.0
20	---	2.5
---	4	5.0
---	16	20
---	40	50
---	80	100
---	120	150
---	160	200

7.3.1.3 For 8260 soil matrix ICAL: Prepare working standards at a minimum of five concentration levels, ranging from 2.5-200 µg/L, by diluting the 50 µg/mL Calibration Intermediate Solution 1. Each ICAL level should contain an equal amount of 400uL methanol . A typical calibration curve would be:

Inter. Solution 1 50 µg/mL (µL/40 mL)	Additional methanol (µL/40 mL)	Final Conc. (µg/L)
2	398	2.5
4	396	5.0
16	384	20
40	360	50
80	320	100
120	280	150
160	240	200

7.3.1.4 ETBE: Prepare working standards at a minimum of six concentration levels, ranging from 2.5-200 µg/L, by diluting the 50 µg/mL Calibration Intermediate Solution 2. A typical calibration curve would be:

Inter. Solution 2 50 µg/mL (µL/40 mL)	Final Conc. (µg/L)
2	2.5
4	5.0
16	20
40	50
80	100
160	200

7.3.1.5 Prepare the calibration standards as directed in the table above. Calibration should be done using the same introduction technique that will be used for the samples. If a sample volume larger than 5 mL is to be used, i.e. 25 mL, the curve should be developed at this volume.

7.3.1.6 The average RF must be calculated using the RF values calculated for each compound from the initial calibration curve. Check the five System Performance Check Compounds (SPCCs) to be sure the minimum RF criteria have been met (see Table 3). If the minimum RFs are not met, a new initial calibration curve must be generated. the system must be evaluated and corrective action taken before sample analysis can begin. Examples of corrective action may include inspecting the system for leaks, checking for errors in standard preparation or degradation of the standard mix, or evaluating the chromatography system for active sites.

7.3.1.7 The percent relative standard deviation should be less than 15% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) must be less than 30%. See Table 4 for the CCCs. If a CCC has a %RSD > 30%, a new initial calibration must be generated.

7.3.1.8 If the %RSD of any compound is 15% or less, then the relative RF is assumed to be constant over the calibration range, and the average relative RF may be used for quantitation. A minimum of five calibration points may be used to define the working range.

7.3.1.9 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/A_{is}) versus concentration using a first order or higher order regression fit of the calibration points. A first order, or linear fit, may be used with a minimum of five calibration points. A second order, or quadratic fit, requires six calibration points. A correlation coefficient of 0.99 or better is required for each curve fit. The analyst should select the regression order that introduces the least error into the quantitation.

7.3.1.10 Calibration curve calculations are found in the QA Manual.

7.3.1.11 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.3.2 Daily GC/MS Calibration

7.3.2.1 The GC/MS tune check standard containing 50 ng of BFB must meet the Table 1 criteria. The standard must be run and meet the criteria every 12 hours.

7.3.2.2 A mid-level calibration standard must be analyzed every 12 hours. The SPCCs must meet the minimum response criteria on Table 3. If the minimum RFs are not met, the system must be evaluated and corrective action taken before sample analysis can begin. Examples of corrective action may include inspecting the system for leaks, checking for errors in standard preparation or degradation of the standard mix, or evaluating the chromatography system for active sites.

7.3.2.3 Use the Calibration Check Compounds to check the validity of the initial calibration. Calculate the percent drift using:

$$\%Drift = \frac{(C_I - C_c)}{(C_I)}(100)$$

C_I = Calibration Check Compound standard concentration
C_c = Measured concentration using selected quantitation method

7.3.2.4 If the percent difference for each CCC is $\leq$ 20%, the initial calibration is assumed to be valid. If the minimum RFs are not met, the system must be evaluated and corrective action taken before sample analysis can begin. Examples of corrective action may include inspecting the system for leaks, checking for errors in standard preparation or degradation of the standard mix, or evaluating the chromatography system for active sites.

7.3.2.5 Evaluate the internal standard responses and retention times. If the retention time changes by more than 30 seconds from the mid-point of the last initial calibration curve or the Extracted Ion Current Profile (EICP) area for any internal standard changes by a factor of two (- 50% to + 100%) from the mid-point of the last initial calibration curve, the chromatographic system must be inspected for malfunctions and corrections made as required before samples can be analyzed.

7.3.2.6 If any of the daily calibration criteria are not met, minor corrective maintenance may be performed on the system and the calibration check standard re-run. If major corrective action is required, such as cleaning the source or replacing the chromatograph column, a new initial calibration needs to be generated before samples could be analyzed.

7.3.2.7 A method blank must be analyzed prior to the analysis of samples. The method blank should not contain target analytes above the reporting limit. If the method blank does contain analytes above the RL the sample batch is reanalyzed, if possible.

7.4 Analysis

7.4.1 GC/MS Conditions:

7.4.1.1 Mass range: 35-300 amu

7.4.1.2 Scan time: approximately 2.6 scans/sec

7.4.1.3 Initial temperature: 35 °C, hold for 4 minutes

7.4.1.4 Temperature program: 35-180 °C at 8 °C/minute

7.4.1.5 Final temperature: 180 °C, hold until at least one minute after the 1,2,3-trichlorobenzene has eluted

7.4.1.6 Injector temperature: 180-250 °C

7.4.1.7 Interface temperature: 250-300 °C

7.4.1.8 Carrier gas: Helium at approximately 0.6 mL/min at constant flow

7.4.1.9 Purge flow: Approximately 40 mL/minute

7.4.1.10 Desorb flow: Approximately 20 mL/minute

7.4.1.11 Split ratio: Approximately 40:1 (HP 5890 Series II GC), Approximately 100:1 (Thermo Focus GC)

7.4.1.12 Purge time: 11 minutes

7.4.1.13 Desorb time: 0.5 minute (Encon sample concentrator), 1 minute (O.I Analytical Eclipse sample concentrator)

7.4.1.14 Desorb temperature: 250 °C (Encon sample concentrator), 190 °C (O.I Analytical Eclipse sample concentrator)

7.4.1.15 Bake time: 10 minutes

7.4.1.16 Bake temperature: 260 °C (Encon sample concentrator), 210 °C (O.I Analytical Eclipse sample concentrator)

7.4.2 All samples must be allowed to warm to ambient temperature before analysis.

7.4.3 Load vials into the auto sampler. Program the method to analyze a 5 mL sample volume and add 1 µL each of the surrogate and internal standard solutions.

7.4.3.1 The auto sampler adds 1 µL of the 250 µg/mL Internal Standard Solution to each 5 mL calibration standard, blank, sample, MS/MSD, and LCS to obtain a 50 µg/L final concentration.

7.4.3.2 The auto sampler adds 1 µL of the 250 µg/mL auto sampler Surrogate Standard to each 5 mL blank, sample, MS/MSD, and LCS to obtain a 50 µg/L final concentration.

7.4.3.3 The auto sampler does not deliver precisely 1µL of surrogate. This amount tends to be either slightly higher or lower after major maintenance in the auto sampler surrogate valve system. An auto sampler surrogate adjustment calibration must be performed each time the auto sampler surrogate valve system has been serviced.

7.4.3.3.1 Run three blanks with the surrogates delivered by auto sampler and three blanks with the surrogates manually injected into 40ml vials of water at 50ug/L.

7.4.3.3.2 Average the auto sampler and 40 mL vial surrogate concentrations.

7.4.3.3.3 Obtain a correction factor by dividing the auto sampler surrogate concentration average by the manual 40 mL surrogate concentration average.

7.4.3.3.4 Multiply the correction factor by the expected concentration. This yields the actual amount delivered by the auto sampler. Use this factor to calculate the actual surrogate recoveries.

7.4.4 For the samples in each analytical batch selected for spiking, add 40 µL of the 50 µg/mL Spike Standard. Final concentration will be 50 µg/L. A typical batch will have an LCS and MS/MSD. LCS/LCSD will be substituted if enough sample is not provided.

NOTE: If running a dual water batch of 624 and 8260B, use 624 spiking amounts.

7.4.5 If the sample concentration exceeds the initial calibration range, dilute the sample and reanalyze.

7.4.6 The pH of water samples is checked after analysis. The pH should be <2. If the pH isn't <2, it should be noted in the client's report.

7.5 Calculation

7.5.1 Qualitative analysis

7.5.1.1 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. Use a mid-level initial calibration standard to obtain standard reference spectra. 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. The relative intensities of the ions should agree within ± 30% between the sample and reference spectrum.

7.5.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification.

7.5.2 Quantitative analysis

7.5.2.1 Quantitate using the internal standard technique. Use the internal standard preceding the analyte (see Table 2). Quantitation is based on the integrated abundance from the EICP of the primary characteristic ion.

7.5.2.2 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the sample may be determined using the average RF from initial calibration data and the following equation:

$$\text{Water Concentration}\ (\mu g/L) = \frac{(A_x)(I_{is})(F)}{(A)(RF)}$$

A_x = Area of characteristic ion being measured
I_{is} = Amount of internal standard injected (µg/L)
F = Dilution factor
A_{is} = Area of characteristic ion for the internal standard
RF = Average response factor for compound being measured

$$\text{Soil Concentration}\ (mg/kg) = \frac{(A_x)(I_{is})(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

A_x, I_{is}, A_{is}, RF = Same as for water
V_t = Volume of the total extract (mL)

V_i = Volume of extract added (mL) for purging
W_s = Weight of sample extracted or purged (g)
D = % dry weight of sample/100, or 1 for wet weight basis

7.5.2.3 Alternatively, the regression line fitted to the initial calibration may be used for the determination of the analyte concentration.

7.5.2.4 Where applicable, an estimate of concentration for noncalibrated components (Tentatively Identified Compounds – TIC) in the sample can be made. The concentration should be reported as an estimate assuming a response factor of 1 using the nearest internal standard.

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, when there is a change in the test method that may affect how the test is performed or when there is a major change in instrumentation. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. The method blank must be less than the reporting limit or the sample batch is reanalyzed if possible. If it is not possible to reanalyze, the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Accuracy control limits are generated for LCS, MS and surrogates. In-house control charts are generated semi-annually, using 20 Percent Recovery points, as follows:

9.3.1.1 Upper and Lower Control Limit = Mean ± 3s

9.3.1.2 Upper and Lower Warning Limit = Mean ± 2s

9.3.1.3 s = Standard deviation

9.3.2 Precision control limits are generated for MS/MSD. LCS/LCSD will be substituted if there isn't enough sample. In-house control charts are generated semi-annually, using 20 RPD points, as follows:

9.3.2.1 Control Limit = Mean + 3s

9.3.2.2 Warning Limit = Mean + 2s

9.3.2.3 s = Standard deviation

9.3.2.4 RPD = Relative Percent Difference

9.3.3 In-house limits are used for compliance, as the method does not list limits. The limits will be reviewed for reasonableness before using them within the laboratory.

9.3.3.1 For permanent gases and compounds eluting after sec-butylbenzene, in-house limits that calculate narrower than 75.0-125% are set to 75.0-125% (i.e. in-house limits = 79.8-126%, limits are set at 75.0-126%). In-house limits that calculate wider than 70.0-130% are set to 70.0-130% (i.e. in-house limits = 65.8-132%, limits are set at 70.0-130%).

9.3.3.2 For 2,2-dichloropropane, in-house limits that calculate narrower than 70.0-130% are set to 70.0-130% (i.e. in-house limits = 79.8-126%, limits are set at 70.0-130%). In-house limits that calculate wider than 60.0-140% are set to 60.0-140% (i.e. in-house limits = 55.8-142%, limits are set at 60.0-140%).

9.3.3.3 For all other parameters, in-house limits that calculate narrower than 80.0-120% are set to 80.0-120% (i.e. in-house limits = 85.8-122%, limits are set at 80.0-122%). In-house limits that calculate wider than 75.0-125% are set to 75.0-125% (i.e. in-house limits = 75.8-132%, limits are set at 75.8-125%).

9.3.3.4 In-house precision limits that calculate narrower than 20% RPD are set to 20% (i.e. in-house limits = 15.3%, limits are set at 20%). In-house precision limits that calculate wider than 25% are set to 25% (i.e. in-house limits = 28.5%, limits are set at 25%).

9.3.4 QC calculations are found in the QA Manual.

9.3.5 LCS, MS/MSD and surrogates are reviewed.

9.3.6 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is re-extracted and/or re-analyzed if possible. If the batch cannot be re-analyzed, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.7 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS may be flagged in the case narrative of the report.

9.3.8 If a sample surrogate is outside the limits, the sample is reanalyzed if possible. If the sample cannot be reanalyzed, the data is flagged next to the actual result in the report.

10. REPORTING

10.1 Soil samples results are reported in mg/kg on a dry weight basis.

10.2 Water sample results are reported in µg/L.

10.3 The reported result is rounded to two significant figures.

10.4 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

12. REFERENCES

12.1 EPA 5000, 5030B, 5035, 8000B (MN), 8000C (AZ), and 8260B

12.2 Vendor equipment manuals

TABLE 1 - BFB Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15-40% of Mass 95
75	30-60% of Mass 95
95	Base peak, 100% Relative Abundance
96	5-9% of Mass 95
173	<2% of Mass 174
174	>50% of Mass 95
175	5-9% of Mass 174
176	>95% But <101% of Mass 174
177	5-9% of Mass 176

TABLE 2 – Volatile Compounds

Compounds	Retention Time (min.)	Primary Ion
Pentafluorobenzene (IS)	7.61	168
Dichlorodifluoromethane	1.90	85
Chloromethane	2.09	50
Vinyl chloride	2.25	62
Bromomethane	2.61	94
Chloroethane	2.73	64
Trichlorofluoromethane	3.13	101
Dichlorofluoromethane	3.04	67
Ethyl Ether	3.50	59
1,1-Dichloroethene	3.83	96
1,1,2-Trichlorotrifluoroethane	3.88	151
Acetone	3.90	58
Allyl chloride	4.41	76
Methylene chloride	4.62	84
trans-1,2-Dichloroethene	5.08	96
MTBE	5.12	73
1,1-Dichloroethane	5.75	63
Ethyl-t-butylether	6.33	87
2,2-Dichloropropane	6.69	77
cis-1,2-Dichloroethene	6.71	96
2-Butanone	6.74	72
Bromochloromethane	7.08	128
THF	7.16	72
Chloroform	7.24	83
1,1,1-Trichloroethane	7.51	97
Carbon tetrachloride	7.78	117
1,1-Dichloropropene	7.77	75
1,4-Difluorobenzene (IS)	8.74	114

TABLE 2 – Volatile Compounds (continued)

Compounds	Retention Time (min.)	Primary Ion
Dibromofluoromethane (surr.)	7.49	113
Toluene-d8 (surr.)	11.11	98
4-Bromofluorobenzene (surr.)	15.53	95
Benzene	8.08	78
1,2-Dichloroethane	8.12	62
Trichloroethene	9.14	95
1,2-Dichloropropane	9.47	63
Dibromomethane	9.66	93
Bromodichloromethane	9.95	83
cis-1,3-Dichloropropene	10.68	75
Methyl Isobutyl Ketone	10.95	85
Toluene	11.21	92
trans-1,3-Dichloropropene	11.59	75
1,1,2-Trichloroethane	11.88	83
Tetrachloroethene	12.12	166
2-Bromo-1-chloropropane (IS)	11.70	77
1,3-Dichloropropane	12.15	76
Dibromochloromethane	12.53	129
1,2-Dibromoethane	12.68	107
Chlorobenzene	13.54	112
1,1,1,2-Tetrachloroethane	13.69	131
Ethylbenzene	13.75	91
m&p-Xylene	13.96	106
o-Xylene	14.63	106
Styrene	14.65	104
Bromoform	14.94	173
1,4-Dichlorobenzene-d4 (IS)	17.56	152
Isopropylbenzene	15.28	105
Bromobenzene	15.76	156
1,1,2,2-Tetrachloroethane	15.81	83
1,2,3-Trichloropropane	15.86	75
n-Propylbenzene	16.01	91
2-Chlorotoluene	16.13	91
4-Chlorotoluene	16.32	91
1,3,5-Trimethylbenzene	16.33	105
tert-Butylbenzene	16.90	119
1,2,4-Trimethylbenzene	16.98	105
sec-Butylbenzene	17.29	105
1,3-Dichlorobenzene	17.44	146
4-Isopropyltoluene	17.56	119
1,4-Dichlorobenzene	17.61	146

TABLE 2 – Volatile Compounds (continued)

Compounds	Retention Time (min.)	Primary Ion
1,2-Dichlorobenzene	18.25	146
n-Butylbenzene	18.29	91
1,2-Dibromo-3-chloropropane	19.64	75
1,2,4-Trichlorobenzene	21.16	180
Hexachlorobutadiene	21.52	225
Naphthalene	21.58	128
1,2,3-Trichlorobenzene	22.02	180

TABLE 3 - System Performance Check Compounds

Compounds	Minimum Response Factor
Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

TABLE 4 – Calibration Check Compounds

Compounds	%RSD
1,1-Dichloroethene	<30
Chloroform	<30
1,2-Dichloropropane	<30
Toluene	<30
Ethylbenzene	<30
Vinyl chloride	<30

Appendix A

Initial Demonstration of Capability (IDC)
Determination of Volatile Organic Compounds by GC/MS

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four replicate standards of the LCS in Ottawa sand and/or lab-grade water and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using form ‘IDC 4 rep with RPD’, the individual recoveries in concentration and %, the mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: LCS limits
   Precision: LCS limits

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee’s personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
Determination of Volatile Organic Compounds by GC/MS

Parameter	Water MDL (µg/L)	Water RL (µg/L)	Soil MDL (mg/kg)	Soil RL (mg/kg)
Dichlorodifluoromethane	0.58	5.0	0.082	0.50
Chloromethane	0.37	2.5	0.041	0.25
Vinyl chloride	0.087	1.0	0.023	0.25
Bromomethane	0.95	5.0	0.14	0.50
Chloroethane	0.46	2.5	0.073	0.25
Trichlorofluoromethane	0.17	1.0	0.032	0.25
*Dichlorofluoromethane	0.31	1.0	0.044	0.25
*Ethyl Ether	0.53	5.0	0.048	0.50
1,1-Dichloroethene	0.12	1.0	0.025	0.25
*1,1,2-Trichlorotrifluoroethane	0.28	1.0	0.065	0.25
*Acetone	2.8	20	0.32	2.0
*Allyl chloride	0.76	5.0	0.067	0.50
Methylene chloride	0.65	5.0	0.17	1.0
trans-1,2-Dichloroethene	0.29	1.0	0.022	0.25
*MTBE	0.13	1.0	0.017	0.25
1,1-Dichloroethane	0.11	1.0	0.024	0.25
^ETBE	---	5.0	---	0.50
2,2-Dichloropropane	0.58	5.0	0.068	0.50
cis-1,2-Dichloroethene	0.19	1.0	0.046	0.25
*2-Butanone	0.67	20	0.12	2.0
Bromochloromethane	0.21	1.0	0.025	0.25
*THF	0.77	20	0.10	2.0
Chloroform	0.19	1.0	0.042	0.25
1,1,1-Trichloroethane	0.17	1.0	0.033	0.25
Carbon tetrachloride	0.16	1.0	0.027	0.25
1,1-Dichloropropene	0.15	1.0	0.027	0.25
Benzene	0.093	1.0	0.015	0.25
1,2-Dichloroethane	0.18	1.0	0.025	0.25
Trichloroethene	0.20	1.0	0.040	0.25
1,2-Dichloropropane	0.21	1.0	0.028	0.25
Dibromomethane	0.30	2.5	0.046	0.25
Bromodichloromethane	0.22	1.0	0.035	0.25
cis-1,3-Dichloropropene	0.16	1.0	0.023	0.25
*Methyl Isobutyl Ketone	1.1	5.0	0.092	0.50

* = Additional compounds from Minnesota list
^ = Additional compounds not found in typical LEGEND 8260B list

Appendix B (continued)

Method Detection Limits and Reporting Limits
Determination of Volatile Organic Compounds by GC/MS

Parameter	Water MDL (µg/L)	Water RL (µg/L)	Soil MDL (mg/kg)	Soil RL (mg/kg)
Toluene	0.21	1.0	0.028	0.25
trans-1,3-Dichloropropene	0.17	1.0	0.035	0.25
1,1,2-Trichloroethane	0.19	1.0	0.037	0.25
Tetrachloroethene	0.20	1.0	0.035	0.25
1,3-Dichloropropane	0.15	1.0	0.017	0.25
Dibromochloromethane	0.50	2.5	0.032	0.25
1,2-Dibromoethane	0.37	2.5	0.038	0.25
Chlorobenzene	0.15	1.0	0.025	0.25
1,1,1,2-Tetrachloroethane	0.28	1.0	0.026	0.25
Ethylbenzene	0.21	1.0	0.022	0.25
m&p-Xylene	0.42	2.0	0.088	0.50
o-Xylene	0.18	1.0	0.031	0.25
Styrene	0.13	1.0	0.040	0.25
Bromoform	0.50	5.0	0.080	0.50
Isopropylbenzene	0.17	1.0	0.023	0.25
Bromobenzene	0.17	1.0	0.019	0.25
1,1,2,2-Tetrachloroethane	0.13	1.0	0.025	0.25
1,2,3-Trichloropropane	0.24	2.5	0.053	0.25
n-Propylbenzene	0.13	1.0	0.014	0.25
2-Chlorotoluene	0.17	1.0	0.018	0.25
4-Chlorotoluene	0.14	1.0	0.029	0.25
1,3,5-Trimethylbenzene	0.18	1.0	0.015	0.25
tert-Butylbenzene	0.19	1.0	0.018	0.25
1,2,4-Trimethylbenzene	0.17	1.0	0.020	0.25
sec-Butylbenzene	0.22	1.0	0.010	0.25
1,3-Dichlorobenzene	0.21	1.0	0.028	0.25
p-Isopropyltoluene	0.30	2.5	0.030	0.25
1,4-Dichlorobenzene	0.17	1.0	0.018	0.25
1,2-Dichlorobenzene	0.16	1.0	0.027	0.25
n-Butylbenzene	0.32	2.5	0.032	0.25
1,2-Dibromo-3-chloropropane	0.60	5.0	0.057	0.50
1,2,4-Trichlorobenzene	0.32	5.0	0.064	0.50
Hexachlorobutadiene	0.76	10	0.13	1.0
Naphthalene	0.40	5.0	0.065	0.50
1,2,3-Trichlorobenzene	0.47	5.0	0.066	0.50

DOCUMENT REVIEW

DOCUMENT:	SOP LABENV-020.6
REVIEWER:	Henrik Pham
DATE:	03/17/09

SECTION	CHANGE	RATIONALE
SOP	Deleted reference to 1,4-Dioxane	1,4-Dioxane no longer a requested analyte
7.3.1.2	Added 'For 8260 water matrix ICAL:' and deleted ' Each ICAL level should contain an equal amount of methanol.'	Water matrix samples and standards do not require methanol addition
7.3.1.3	Inserted subsection to address 8260 soil matrix ICAL preparation	Soil matrix ICAL different from water matrix ICAL preparation
Appendix B	Updated Water RLs for Bromomethane, Methylene chloride, 1,1,1-trichloroethane, and Carbon tetrachloride	MDL study shows RLs can be lowered
Appendix B	Updated MDLs	Annual update
Document Review	Updated form	Revised form

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF SEMI-VOLATILE COMPOUNDS IN SOIL/SOLID BY GC/MS

SOP NO.: LABENV-021.9

Original Information		
Prepared by:	Sandy McDonald	Date: 03/13/96
Technical Review:		Date:
QA/QC Coordinator:	Sharon Cenis	Date: 03/25/96
Authorized by:	Cheryl Sykora	Date: 03/29/96

Revision Information		
Supersedes:	LABENV-021.8	Date: 04/07/08
Revised by:	Van Pham	Date: 03/17/09
Signature:	______________________	Date: __________
Technical Review:	Triet Le	Date: 03/17/09
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 03/17/09
Signature:	______________________	Date: __________

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Signature:	[signature]	Date: 3/17/09
Technical Review:	Triet Le	Date:
Signature:	[signature]	Date: 3/17/09
Authorized by:	Cheryl Sykora	Date:
Signature:	[signature] Cheryl Sykora	Date: 3/17/09

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FORM GEN-021 (05/07)

SOP TITLE: DETERMINATION OF SEMI-VOLATILE COMPOUNDS IN SOIL BY GC/MS

1. PURPOSE

1.1 This document defines the preparation and analysis for semi-volatile compounds in soil and solid matrices by Gas Chromatography/Mass Spectrometry (GC/MS). This procedure can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. The SOP is applicable to samples typically analyzed by EPA 8270C.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in this SOP.

2.3 An analyst experienced in the use of gas chromatograph/mass spectrometers, skilled in the interpretation of mass spectra, and trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This method is applicable to soil/solid samples only.

3.2 The Sonication Method may be used when a sample has the potential to be detrimental to the ASE (e.g. tar samples, fine sediments, etc.).

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard and exposure to these chemicals minimized.

4.3 Follow standard laboratory safety procedures.

4.4 A lab coat and safety glasses should be worn during sample and standard preparation.

4.5 When working with organic compounds, wear chemical resistant gloves.

4.6 Prepare stock and standard solutions in a hood.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Soil samples should be collected in unweighed 4 oz. glass jars with Teflon-lined caps and stored at 4 ± 2 ºC.

5.3.1 Soil/sediment samples – Decant and discard any water layer. Mix thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

5.3.2 Dry waste samples – Grind so that sample may pass through a 1 mm sieve. Grind enough sample to yield at least 15 grams.

5.4 The recommended holding time for soil samples is 14 days until extraction and analysis within 40 days of extraction.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 HP 5890 Series II Gas Chromatograph (GC) with data processing equipment, or equivalent

6.2 HP 5972A Mass Selective Detector (MSD) with scan range of 35 to 500 amu using 70 volts electron energy in the electron impact ionization mode, or equivalent

6.3 Column – 30m x 0.25 mm ID (or 0.32 mm ID) 0.25 µm film thickness silicone-coated fused silica capillary column (DB-5MS or equivalent)

6.4 Nitrogen evaporator – N-EVAP, or equivalent

6.5 Ultrasonic Disrupter - Bronson Sonifier 450, or equivalent

6.6 Microliter syringes – 10, 25, 100, 250, 500, and 1000 µL

6.7 Volumetric flasks – 5, 10, 25, and 50 mL

6.8 Serum Bottles – amber glass with Teflon-lined crimp tops

6.9 Beaker – 400mL

6.10 Glass funnel with Pyrex glass wool at bottom

6.11 Side arm vacuum flask – 500 mL

6.12 Buchner funnel

6.13 Filter paper - Whatman No. 41 or equivalent

6.14 Kuderna-Danish (K-D) concentrator – 10 mL, graduated

6.15 Kuderna-Danish (K-D) flask – 500 mL

6.16 Snyder column – three ball macro

6.17 PTFE solvent rinsed boiling beads, or equivalent

6.18 Water bath

6.19 Autosampler vials – 2 mL amber glass with Teflon lined crimp tops

6.20 Graduated disposable pipets – 1 or 2 mL

6.21 Mortar and pestle, or equivalent

6.22 Balance, capable of reading to 0.01 g

6.23 Turbo Vap II and associated parts and glassware

6.24 Accelerated Solvent Extractor (ASE) and associated parts and glassware

6.25 Disposable aluminum weighing dishes – prerinsed with hexane and methylene chloride

6.26 Anhydrous Sodium Sulfate (Na_2SO_4) – muffle at 400 °C for four hours before using

6.27 Ottawa Sand (20-30 mesh) or equivalent – muffle at 400 °C for four hours before using

6.28 Hydromatrix® – muffle at 400 °C for four hours before using

6.29 Methanol – pesticide grade, or equivalent

6.30 Methylene chloride, CH_2Cl_2 – pesticide grade, or equivalent

6.31 Acetone – pesticide grade, or equivalent

6.32 Methylene chloride/Acetone (1:1) (v/v) – for sonication preparation technique

6.33 Methylene chloride/Acetone (3:1) (v/v) – for ASE preparation technique

6.34 GC/MS Tune Check Stock – 500 µg/mL each of DFTPP, Benzidine, 4.4'-DDT, and pentachlorophenol, Absolute Standards, Inc. #43030, or equivalent

6.35 Calibration Stock 1 – 2000 µg/mL each of bis(2-chloroethoxy) methane, bis(2-chloroethyl) ether, bis(2-ethylhexyl) phthalate, bis(2-chloroisopropyl)ether, 4-bromophenyl phenyl ether, butyl benzyl phthalate, 4-chlorophenyl phenyl ether, diethyl phthalate, dimethyl phthalate, di-n-butyl phthalate, di-n-octyl phthalate, n-nitrosodimethylamine, n-nitrosodi-n-propylamine, and n-nitrosodiphenylamine, Absolute #10001, or equivalent

6.36 Calibration Stock 2 – 2000 µg/mL each of acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, carbazole, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene Absolute #10007, or equivalent

6.37 Calibration Stock 3 – 2000 µg/mL each of azobenzene (1,2-diphenylhydrazine), 2-chloronaphthalene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, 1,3 dichlorobenzene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclopentadiene, hexachloroethane, isophorone, nitrobenzene, and 1,2,4-trichlorobenzene, Absolute #10002, or equivalent

6.38 Calibration Stock 4 – 2,000 µg/mL each of aniline, benzyl alcohol, 4-chloroaniline, dibenzofuran, 2-methylnaphthalene, 2-nitroaniline, 3-nitroaniline, and 4-nitroaniline, Absolute #10005, or equivalent

6.39 Calibration Stock 5 – 2,000 µg/mL each of benzoic acid, 2-methylphenol, 4-methylphenol, and 2,4,5-trichlorophenol, Absolute #10004, or equivalent

6.40 Calibration Stock 6 – 2,000 µg/mL each of 4-chloro-3-methylphenol, 2-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4-dimethylphenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 2-nitrophenol, 4-nitrophenol, pentachlorophenol, phenol, 2,4,6-trichlorophenol, and 2,3,4,6-tetrachlorophenol, Absolute #10018, or equivalent

6.41 Calibration Stock 7 – 2,000 µg/mL each of benzidine and 3,3'-dichlorobenzidine, Absolute #10006, or equivalent

6.42 Calibration Stock 8 – 1,000 µg/mL of pyridine, Absolute #70260, or equivalent

6.43 Internal Standard Stock – 4,000 µg/mL each of acenaphthene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, naphthalene-d_8, perylene-d_{12}, and phenanthrene-d_{10}, Absolute #10009, or equivalent

6.44 Calibration Surrogate Stock 1 – 10,000 µg/mL each of 2-flurophenol, phenol-d6, and 2,4,6-tribromophenol, Absolute #21015, or equivalent

6.45 Calibration Surrogate Stock 2 – 5,000 µg/mL each of nitrobenzene-d_5, 2-fluorobiphenyl, and terphenyl-$d_{14,}$ Absolute #21016, or equivalent

6.46 Sample/Second Source Surrogate Stock 1 – 10,000 µg/mL each of 2-flurophenol, phenol-d6, and 2,4,6-tribromophenol, Restek #31087, or equivalent

6.47 Sample/Second Source Surrogate Stock 2 – 5,000 µg/mL each of nitrobenzene-d_5, 2-fluorobiphenyl, and terphenyl-$d_{14,}$ Restek #31086, or equivalent

6.48 Spike Stock 1 – 10,000 µg/mL each of pentachlorophenol, phenol, 2-chlorophenol, 4-chloro-3-methylphenol, and 4-nitrophenol, Restek #31071, or equivalent

6.49 Spike Stock 2 – 5,000 µg/mL each of 1,2,4-trichlorobenzene, acenaphthene, 2,4-dinitrotoluene, pyrene, n-nitrosodi-n-propylamine, and 1,4-dichlorobenzene, Restek #31084, or equivalent

6.50 Spike Stock 3 – 2,000 µg/mL each of acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, 2-methylnaphthalene, naphthalene, phenanthrene, and pyrene, Absolute #50003, or equivalent

6.51 Second Source Stock 9 - 1000ug/ml of all 8270 components except for benzidine, 3,3'-dichlorobenzidine, 2,6-dichlorophenol, surrogates, and benzoic acid , Restek # 31850 or equivalent

6.52 Second Source Stock 10 - 2000ug/ml each of benzidine and 3,3'-dichlorobenzidine, Restek # 31834 or equivalent

6.53 Second Source Stock 11 - 1000ug/ml of 2,6-dichlorophenol, Restek # 31409 or equivalent

6.54 Second source stock 12 - 1000ug/ml of benzoic acid, Absolute #70034, or equivalent

6.55 Calibration Intermediate Solution – combine 300 µL of the 2,000 µg/mL Calibration Stocks 1-7, 600 µL of the 1,000 µg/mL Calibration Stock 8, 60 µL of the 10,000 µg/mL Surrogate Stock 1, 120 µL of the 5,000 µg/mL Surrogate Stock 2, and 120 µL of methylene chloride (3 mL final volume) to produce a 200 µg/mL Calibration Intermediate Solution

6.56 GC/MS Tune Check Standard – dilute 100 µL of the 500 µg/mL GC/MS Tune Check Stock with 900 µL of methylene chloride to produce a 50 µg/mL GC/MS Tune Check Standard

6.57 Sample Surrogate Standard – dilute 0.5 mL of the 10,000 µg/mL Surrogate Stock 1 and 1 mL of the 5,000 µg/mL Surrogate Stock 2 to a final volume of 50 mL with methanol to produce a 100 µg/mL Sample Surrogate Standard

6.58 Spike Standard – dilute 0.5 mL of the 10,000 µg/mL Spike Stock 1, 1 mL of the 5,000 µg/mL Spike Stock 2, and 2.5 mL of the 2,000 µg/mL Spike Stock 3 to a final volume of 50 mL with methanol to produce a 100 µg/mL Spike Standard

6.59 Second Source ICV - combine 50 µL of the 1,000 µg/mL Stocks 9, 11 and 12, 25 µL of the 2000 µg/mL Stock 10, 5.0 µL of the 10,000 µg/mL Sample Surrogate Stock 1, 10 µL of the 5,000 µg/mL Sample Surrogate Stock 2, and 810 µL of methylene chloride (1 mL final volume) to produce a 50 µg/mL Second Source Calibration Solution. Add 10 µL of the 4,000 µg/mL Internal Standard Stock prior to analysis to produce an ISTD concentration of 40 µg/mL.

6.60 All solutions and standards should be stored in a freezer at ≤ -10 ºC and should be freshly prepared each year, or sooner if check standards or continuing calibration standards indicate a problem.

7. PROCEDURE

7.1 Preparation of Samples – ASE Technique

7.1.1 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

7.1.2 Assemble extraction cell by screwing a cell end cap onto cell body

7.1.3 Place 2 filters on top of the open end of the cell body. Use the black cylindrical insertion tool to push the filters to the bottom of the assembled cell body. Very fine soils may require three filters.

7.1.4 Weigh approximately 15 g of sample into a prerinsed disposable aluminum dish. Record the weight to the nearest 0.01g on the extraction sheet.

7.1.5 Use a 1:1 Ottawa Sand:Hydromatrix® mixture for the blank and Laboratory Control Sample (LCS). A typical batch will have an LCS and MS/MSD. LCS/LCSD will be substituted if enough sample is not provided.

7.1.6 Mix the sample with Hydromatrix®, or equivalent, using approximately a 1:1 ratio by volume, until free-flowing. Depending on the matrix, the amount of sample may need to be reduced.

7.1.7 Place the extraction cell funnel on open end of cell body. Load sample into cell through funnel. Gently tap cell on hard surface to pack sample evenly, and to reduce void volume.

7.1.8 All samples should come within 1 cm of the top of the vessel. If a sample does not, use sand to fill.

7.1.9 When the transfer is complete, remove the funnel. Add 1.0 mL of the 100 µg/mL Sample Surrogate Standard to each sample, blank, and spike sample. Final concentration will be 6.67 mg/kg, assuming a 1.0 mL final volume, 1 µL injection, and 15 g sample amount.

7.1.10 For the samples in each analytical batch selected for spiking, add 1.0 mL of the 100 µg/mL Spike Standard. Final concentration will be 6.67 mg/kg, assuming a 1.0 mL final volume, 1 µL injection, and 15 g sample amount.

7.1.11 Place filter paper on top of the sample. Remove any debris from cell threads and screw the second end cap onto open end of the cell body.

7.1.12 Place completed extraction cell into position #1 on the ASE. Place the corresponding collection vial into position #1 below.

7.1.13 Repeat the above steps for additional samples.

7.1.14 Fill solvent bottle with the 3:1 methylene chloride:acetone. Record their lot numbers on the solvent bottle.

7.1.15 Make sure pressure on gas tank is set to 180 psi. Make sure that solvent bottle pressure is 10 psi, system air pressure is 50 psi, and compression oven pressure is 130 psi. Record the pressure readings in the soil extraction log.

7.1.16 After the ASE extraction, assemble a K-D apparatus by attaching a 10 mL K-D concentrator to a 500 mL K-D flask for Nitrogen Blowdown or a 200 mL Turbo Vap II concentration vial. The Nitrogen Blowdown technique is used when there is over 200 mL of extract.

7.1.17 Decant extraction solvent through a methylene chloride rinsed funnel filled one-third full with sodium sulfate and plugged with glass wool. Rinse the collection vial three times with methylene chloride to complete quantitative transfer. Collect the extract in the assembled K-D apparatus or a 200 mL Turbo Vap II concentration vial.

7.1.18 K-D Technique / Nitrogen Blowdown

7.1.18.1 Add one solvent rinsed boiling bead to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-85 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot vapor. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

7.1.18.2 When the apparent volume of liquid reaches 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool. Remove the Snyder column.

7.1.18.3 Put the K-D concentrator in a warm bath (35 ºC) and evaporate the solvent volume to less than 1 mL using a gentle stream of clean, dry nitrogen. During evaporation, the tube solvent level must be positioned to avoid water condensation (i.e. the solvent level should be below the level of the water bath). Do not allow the extract to go dry as this may result in a loss of analytes. Using a disposable graduated pipet, adjust the final volume to 1.0 mL with methylene chloride and mix the extract completely.

7.1.18.4 Transfer to a 2 mL autosampler vial. Store in freezer until analysis.

7.1.19 Turbo Vap II

7.1.19.1 Place the Turbo Vap collection tube in the Turbo Vap.

7.1.19.2 Set the water bath temperature to 40 °C and the pressure to 8-12 psi.

7.1.19.3 Set the Turbo Vap to monitor by ‘sensor’ to achieve a final volume of approximately 1 mL.

7.1.19.4 Using a graduated disposable pipet, adjust the final volume to 1.0 mL with methylene chloride and mix the extract completely.

7.1.19.5 Transfer to a 2 mL autosampler vial. Store in freezer until analysis.

7.2 Preparation of Samples – Sonication Technique

7.2.1 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

7.2.2 Weigh approximately 15 g of sample into a prerinsed 250 mL beaker. Record the weight to the nearest 0.01 g on the extraction sheet.

7.2.3 Add approximately 15 g of anhydrous muffled Na_2SO_4 and mix the sample well. More sodium sulfate may be added until the sample is free flowing.

7.2.4 Add 1.0 mL of the 100 µg/mL Sample Surrogate Standard to each sample, blank, and spike sample. Final concentration will be 6.67 mg/kg, assuming a 1.0 mL final volume, 1 µL injection, and 15 g sample amount.

7.2.5 For the samples in each analytical batch selected for spiking, add 1.0 mL of the 100 µg/mL Spike Standard. Final concentration will be 6.67 mg/kg, assuming a 1.0 mL final volume, 1 µL injection, and 15 g sample amount. A typical batch will have an LCS and MS/MSD. LCS/LCSD will be substituted if enough sample is not provided.

7.2.6 Immediately add 100 mL of 1:1 methylene chloride/acetone.

7.2.7 Place the bottom surface of the tip of the 2" disrupter horn about 2" below the surface of the solvent, but above the soil/sediment layer.

7.2.8 Extract ultrasonically for about 3 minutes, with output control knob set at 10, mode switch on Pulse and percent-duty cycle knob set at 50%.

7.2.9 Quantitatively transfer the solvent into a glass funnel containing a filter paper and sitting atop a 500 mL K-D apparatus. Repeat steps above with two additional fresh portions of 1:1 methylene chloride/acetone.

7.2.10 K-D Technique / Nitrogen Blowdown

7.2.10.1 Add one solvent rinsed boiling bead to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-85 ºC) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot vapor. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

7.2.10.2 When the apparent volume of liquid reaches 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool. Remove the Snyder column.

7.2.10.3 Put the concentrator tube in a warm bath (35 °C) and evaporate the solvent volume to less than 1 mL using a gentle stream of clean, dry nitrogen. During evaporation, the tube solvent level must be positioned to avoid water condensation (i.e. the solvent level should be below the level of the water bath). Do not allow the extract to go dry as this may result in a loss of analytes. Using a disposable graduated pipet, adjust the final volume to 1.0 mL with methylene chloride and mix the extract completely.

7.2.10.4 Transfer to a 2 mL autosampler vial. Store in freezer until analysis.

7.3 Calibration

7.3.1 Initial Calibration

7.3.1.1 The GC/MS must be tuned to meet the criteria in Table 1 for a 50 ng injection of DFTPP. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachorophenol should be present at their normal responses, and no peak tailing should be visible.

7.3.1.2 Use the base peak ion from the specific internal standard as the primary ion for quantitation, unless interferences are noted.

7.3.1.3 Prepare working standards at a minimum of 5 concentration levels, ranging from 5.0-150 µg/mL (except benzo(k)fluoranthene and benzo(g,h,i)perylene range from 5.0-100 µg/mL, and pentachlorophenol ranges from 10-150 µg/mL), by diluting the 200 µg/mL Calibration Intermediate Solution with methylene chloride. A typical calibration curve would be:

Calib. Inter. Solution (µL/1 mL)	Concentration (µg/mL)
25	5.0
50	10
100	20
250	50
500	100
750	150

7.3.1.4 Add 10 µL of the 4,000 µg/mL Internal Standard Stock to each calibration standard prior to analysis to produce an ISTD concentration of 40 µg/mL.

7.3.1.5 Calculate response factors (RFs) for each compound at each level relative to the preceding internal standard (see Table #2).

7.3.1.6 The average response factor should be calculated for each compound. The percent relative standard deviation (%RSD) should be less than 15% for each compound. However, the %RSD for each Calibration Check Compound (CCC), (see Table 3), must be less than 30%. If these criteria cannot be met, corrective action must be taken and the system recalibrated. Possible problems include standard mixture degradation, injection port inlet contamination, contamination of the front end of the column, or active sites in the column or chromatographic system.

7.3.1.7 System Performance Check Compounds (SPCC) must meet minimum average response factor criteria (see Table 4) or corrective action must be taken. For examples of corrective action, see above.

7.3.1.8 If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation. A minimum of five calibration points may be used to define the working range.

7.3.1.9 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/A_{is}) versus concentration using first order regression fit. Second order (quadratic) curves may be constructed for some compounds that respond poorly in the chromatographic system (e.g. benzyl alcohol, benzoic acid, benzidine, phenol, 4-nitrophenol, 2,3,4,6-tetrachlorophenol, 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol, 2,4,6-tribromophenol, pentachlorophenol, hexachlorocyclopentadiene, acenaphthylene, diethyl phthalate, naphthalene, 2-methylnaphthalene, 2-chloronaphthalene, fluorene, benzo[b] & [k]fluoranthene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene). Second order fit may not be used in place of instrument maintenance. A correlation coefficient of 0.99 or better is required for each curve fit.

7.3.1.10 Immediately after an initial calibration curve is generated it must be verified by a second source verification standard. Acceptance criteria will be set at 70.0 – 130%.

7.3.1.11 Calibration curve calculations are found in the QA Manual.

7.3.1.12 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% (± 50% for AZ samples) or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.3.2 Daily GC/MS calibration

7.3.2.1 The GC/MS tuning standard containing 50 ng of DFTPP must meet the Table 1 criteria. This standard must be run and meet these criteria every 12 hours.

7.3.2.2 A mid-level calibration standard must be analyzed every 12 hours. Two different concentrations of CCVs will be used to verify quadratic calibration curves when analyzing WI compliance samples. The SPCCs must meet the minimum response criteria on Table 4.

7.3.2.3 Use the Calibration Check Compounds (CCCs), found in Table 3, to check the validity of the initial calibration. Calculate the percent drift using:

$$\%Drift = \frac{(C_I - C_c)}{(C_I)}(100)$$

C_I = Calibration Check Compound standard concentration
C_c = Measured concentration using selected quantitation method

If the percent difference for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. Non-CCC must meet the acceptance criteria of ≤ 20% for Arizona compliance samples.

7.3.2.4 Evaluate the internal standard responses and retention times. If the retention time changes by more than 30 seconds from the mid-point of the last initial calibration curve or the Extracted Ion Current Profile (EICP) area for any internal standard changes by a factor of two (- 50% to + 100%) from the mid-point of the last initial calibration curve, the chromatographic system must be inspected for malfunctions and corrections made as required before samples can be analyzed.

7.3.2.5 If any of the daily calibration criteria are not met, minor corrective maintenance may be performed on the system and the calibration check standard re-run. If major corrective action were required, such as cleaning the source or replacing the chromatographic column, a new initial calibration would need to be generated before samples could be analyzed.

7.4 Analysis

7.4.1 GC/MS Conditions

7.4.1.1 Mass Range: 35-500 amu

7.4.1.2 Scan Time: approximately 1 scan/sec

7.4.1.3 Initial Temperature: 40 °C, hold for 4 minutes

7.4.1.4 Temp. Program: 40-320 °C at 10 °C/min

7.4.1.5 Final Temperature: 320 °C, hold until at least one minute after benzo(g,h,i)perylene has eluted

7.4.1.6 Injector Temperature: 250-300 °C

7.4.1.7 Interface Temperature: 250-300 °C

7.4.1.8 Injector: Split/Splitless

7.4.1.9 Sample volume: 1 µL

7.4.1.10 Carrier gas: Helium at 1 mL/min

7.4.2 Add 10 µL of the 4,000 µg/mL Internal Standard Stock to each sample extract to produce an ISTD concentration of 40 µg/mL.

7.4.3 Inject 1 µL of the 1 mL sample extract. If the response for any quantitation ion exceeds the initial calibration curve, make an appropriate dilution, add additional internal standard as required to maintain 40 µg/mL of each internal standard. Reanalyze the diluted extract.

7.4.4 Recap samples prior to storing in freezer.

7.5 Calculation

7.5.1 Qualitative analysis

7.5.1.1 The retention time of the sample compound must fall within ± 30 seconds of the retention time of the standard compound run within the last 12 hours.

7.5.1.2 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. Use the continuing calibration standard to obtain standard reference spectra.

7.5.1.3 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. The relative intensities of the ions should agree within ± 30% between the sample and reference spectrum.

7.5.1.4 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification.

7.5.2 Quantitative analysis

7.5.2.1 Quantitate using the internal standard technique. Use the internal standard preceding the analyte (see Table 2). Quantitation is based on the integrated abundance from the EICP of the primary characteristic ion.

7.5.2.2 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data and the following equation:

$$Concentration\left(mg/kg\right)=\frac{(A_x)(C_{is})(F)(V_{ex})}{(A_{is})(RF)(W_s)(D)}$$

A_x = Area of characteristic ion being measured
C_{is} = Amount of internal standard injected (µg/mL)
F = Dilution factor
V_{ex} = Volume of extract, mL
A_{is} = Area of characteristic ion for the internal standard
RF = Mean response factor for compound being measured
W_s = Weight of sample extracted, g
D = % dry weight of sample/100, or 1 for wet weight basis

7.5.2.3 Alternatively, the regression line fitted to the initial calibration may be used for the determination of the analyte concentration. Compute the concentration of the analyte in the sample using the following equation:

$$Concentration\,(mg/kg)=\frac{(C_{ex})(V_{ex})}{(W_s)(D)}$$

C_{ex} = extract concentration, µg/mL
V_{ex} = extract volume, mL
W_s = sample weight, g
D = % dry weight of sample/100, or 1 for wet weight basis

7.5.2.4 Where applicable, an estimate of concentration for noncalibrated components in the sample can be made. The concentration should be reported as an estimate assuming a response factor of 1 using the nearest internal standard.

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, when there is a change in the test method that may affect how the test is performed or when there is a major change in instrumentation. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. The method blank must be less than the reporting limit or the sample batch is re-extracted if possible. If it is not possible to re-extract, the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Accuracy control limits are generated for LCS, MS and surrogates. In-house control charts are generated semi-annually, using 20 Percent Recovery points, as follows:

9.3.1.1 Upper and Lower Control Limit = Mean ± 3s

9.3.1.2 Upper and Lower Warning Limit = Mean ± 2s

9.3.1.3 s = Standard deviation

9.3.1.4 For Arizona compliance, the lower control limit can not calculate below the lowest standard on the calibration curve (e.g. lowest standard = 5.0 µg/mL, spike is at 100 µg/mL, % can not be below 5.0%). The Minnesota Pollution Control Agency sets a guideline that the lower control limit can not be < 30.0%. LEGEND will use the greater of these two; 30.0% in this example.

9.3.2 Precision control limits are set at 20.0% RPD for LCS/LCSD and generated for MS/MSD. In-house control charts are generated semi-annually, using 20 RPD points, as follows:

9.3.2.1 Control Limit = Mean + 3s

9.3.2.2 Warning Limit = Mean + 2s

9.3.2.3 s = Standard deviation

9.3.2.4 RPD = Relative Percent Difference

9.3.3 QC calculations are found in the QA Manual.

9.3.4 LCS, MS and surrogates are reviewed.

9.3.5 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is re-extracted and/or re-analyzed if possible. If the batch cannot be re-extracted and/or re-analyzed, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.6 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS is flagged and/or a case narrative is written.

9.3.7 If a sample surrogate is outside the limits, the sample is re-extracted and/or reanalyzed if possible. If the sample cannot be re-extracted and/or reanalyzed, the data is flagged next to the actual result in the report.

10. REPORTING

10.1 Soil samples results are reported in mg/kg on a dry weight basis.

10.2 The reported result is rounded to two significant figures.

10.3 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

12. REFERENCES

12.1 EPA 3500B, 3550B, 3545, 8270C, 8000B (MN), 8000C (AZ)

12.2 Vendor equipment manuals

TABLE 1 - DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	10-80% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	10-80% of mass 198
197	< 2% of mass 198
198	Base peak or >50% of 442
199	5-9% of mass 198
275	10-60% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	Base peak or > 50% of mass 198
443	15-24% of mass 442

TABLE 2 – Semi-Volatile Compounds

Compound	Primary Ion
1,4-Dichlorobenzene-d_4(IS)	152
n-Nitrosodimethylamine	74
2-Fluorophenol (surr.)	112
Aniline	93
bis(2-Chloroethyl)ether	93
Phenol-d_6 (surr.)	99
Phenol	94
2-Chlorophenol	128
1,3-Dichlorobenzene	146
1,4-Dichlorobenzene	146
1,2-Dichlorobenzene	146
Benzyl alcohol	108
bis(2-Chloroisopropyl)ether	45
2-Methylphenol	108
Hexachloroethane	117
N-Nitrosodi-n-propylamine	70
4-Methylphenol	108
Naphthalene-d_8 (IS)	136
Nitrobenzene-d_5 (surr.)	82

TABLE 2 – Semi-Volatile Compounds (continued)

Compound	Primary Ion
Nitrobenzene	77
Isophorone	82
2-Nitrophenol	139
2,4-Dimethylphenol	107
bis(2-Chloroethoxy)methane	93
2,4-Dichlorophenol	162
1,2,4-Trichlorobenzene	180
Naphthalene	128
Benzoic acid	122
2,6-Dichlorophenol	162
4-Chloroaniline	127
Hexachlorobutadiene	225
4-Chloro-3-methylphenol	107
2-Methylnaphthalene	142
Acenaphthene-d_{10} (IS)	164
Hexachlorocyclopentadiene	237
2,4,6-Trichlorophenol	196
2,4,5-Trichlorophenol	196
2-Fluorobiphenyl (surr.)	172
2-Chloronaphthalene	162
2-Nitroaniline	65
Acenaphthylene	152
Dimethylphthalate	163
2,6-Dinitrotoluene	165
Acenaphthene	153
3-Nitroaniline	138
2,4-Dinitrophenol	184
Dibenzofuran	168
2,4-Dinitrotoluene	165
4-Nitrophenol	109
2,3,4,6-Tetrachlorophenol	232
Fluorene	166
4-Chlorophenyl-phenylether	204
Diethylphthalate	149
4-Nitroaniline	138

TABLE 2 – Semi-Volatile Compounds (continued)

Compound	Primary Ion
Phenanthrene-d_{10} (IS)	188
4,6-Dinitro-2-methylphenol	198
N-Nitrosodiphenylamine	169
Azobenzene	77
2,4,6-Tribromophenol (surr.)	330
4-Bromophenyl-phenylether	248
Hexachlorobenzene	284
Pentachlorophenol	266
Phenanthrene	178
Anthracene	178
Carbazole	167
Di-n-butylphthalate	149
Fluoranthene	202
Chrysene-d_{12} (IS)	240
Benzidine	184
Pyrene	202
Terphenyl-d_{14} (surr.)	244
Butylbenzylphthalate	149
3,3'-Dichlorobenzidine	252
Benzo[a]anthracene	228
Chrysene	228
bis(2-Ethylhexyl)phthalate	149
Perylene-d_{12} (IS)	264
Di-n-octylphthalate	149
Benzo[b]fluoranthene	252
Benzo[k]fluoranthene	252
Benzo[a]pyrene	252
Indeno[1,2,3-cd]pyrene	276
Dibenz[a,h]anthracene	278
Benzo[g,h,i]perylene	276

TABLE 3 - Calibration Check Compounds

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE 4 - System Performance Check Compounds

Compounds	Minimum Response Factor
N-Nitroso-di-n-propylamine	0.050
Hexachlorocyclopentadiene	0.050
2,4-Dinitrophenol	0.050
4-Nitrophenol	0.050

Appendix A

Initial Demonstration of Capability (IDC)
Semi-volatile Organic Compounds (SVOC)

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards in Ottawa Sand and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: LCS limits
   Precision: LCS limits

   If the standards were not extracted, the results must meet the following criteria:

   Accuracy: 80.0-120%
   Precision: ≤ 20% RPD

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
Semi-volatile Organic Compounds (SVOC)

Parameter	MDL (mg/kg)	RL (mg/kg)	Parameter	MDL (mg/kg)	RL (mg/kg)
1,2,4-Trichlorobenzene	0.027	0.33	Benzo(a)pyrene	0.027	0.33
1,2-Dichlorobenzene	0.025	0.33	Benzo(b)fluoranthene	0.034	0.33
1,3-Dichlorobenzene	0.023	0.33	Benzo(k)fluoranthene	0.031	0.33
1,4-Dichlorobenzene	0.024	0.33	Benzo(g,h,i)perylene	0.030	0.33
2,3,4,6-Tetrachlorophenol	0.038	0.67	Benzoic Acid	0.032	0.33
2,4,5-Trichlorophenol	0.024	0.67	Benzyl Alcohol	0.12	0.67
2,4,6-Trichlorophenol	0.035	0.67	bis(2-Chloroethoxy)methane	0.021	0.33
2,4-Dichlorophenol	0.035	0.67	bis(2-Chloroethyl)ether	0.024	0.33
2,4-Dimethylphenol	0.090	0.67	bis(2-Chloroisopropyl)ether	0.022	0.33
2,4-Dinitrophenol	0.058	0.67	bis(2-Ethylhexyl)phthalate	0.020	0.33
2,4-Dinitrotoluene	0.021	0.33	Butylbenzylphthalate	0.021	0.33
2,6-Dichlorophenol	0.043	0.67	Carbazole	0.022	0.33
2,6-Dinitrotoluene	0.019	0.33	Chrysene	0.023	0.33
2-Chloronaphthalene	0.019	0.33	Dibenz(a,h)anthracene	0.034	0.33
2-Chlorophenol	0.038	0.67	Dibenzofuran	0.019	0.33
2-Methylnaphthalene	0.028	0.33	Diethylphthalate	0.015	0.33
2-Methylphenol	0.035	0.67	Dimethylphthalate	0.018	0.33
2-Nitroaniline	0.020	0.33	Di-n-butylphthalate	0.037	0.33
2-Nitrophenol	0.036	0.67	Di-n-octylphthalate	0.025	0.33
3,3'-Dichlorobenzidine	0.39	1.6	Fluoranthene	0.024	0.33
3-Nitroaniline	0.033	0.33	Fluorene	0.018	0.33
4,6-Dinitro-2-methylphenol	0.074	0.67	Hexachlorobenzene	0.016	0.33
4-Bromophenyl-phenylether	0.017	0.33	Hexachlorobutadiene	0.033	0.33
4-Chloro-3-methyl phenol	0.040	0.67	Hexachlorocyclopentadiene	0.041	0.33
4-Chloroaniline	0.11	0.67	Hexachloroethane	0.028	0.33
4-Chlorophenyl-phenylether	0.023	0.33	Indeno(1,2,3-cd)pyrene	0.032	0.33
4-Methylphenol	0.027	0.67	Isophorone	0.017	0.33
4-Nitroaniline	0.023	0.33	Naphthalene	0.025	0.33
4-Nitrophenol	0.099	0.67	Nitrobenzene	0.030	0.33
Acenaphthene	0.028	0.33	n-Nitrosodimethylamine	0.032	0.33
Acenaphthylene	0.023	0.33	n-Nitrosodi-n-propylamine	0.025	0.33
Aniline	0.090	0.67	n-Nitrosodiphenylamine	0.018	0.33
Anthracene	0.025	0.33	Pentachlorophenol	0.096	0.67
Azobenzene (1,2-Diphenylhydrazine)	0.020	0.33	Phenanthrene	0.019	0.33
Benzidine	0.13	2.5	Phenol	0.057	0.67
Benzo(a)anthracene	0.027	0.33	Pyrene	0.014	0.33

DOCUMENT REVIEW

DOCUMENT:	SOP LABENV-021.9
REVIEWER:	Van Pham
DATE:	02/04/09

SECTION	CHANGE	RATIONALE
6.46 & 6.47	Added 'Second Source'	Added second source standard
6.51 → 6.54, 6.59	Added second source standards	Second source standard required
7.3.1.9	Added naphthalene, 2-methylnaphthalene, 2-chloronaphthalene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene to list of analytes that may use quadratic fit	Identified as poorly responding compounds
7.3.10	Inserted subsection	Wisconsin requirement
7.3.2.2	Added 'Two different concentrations of CCVs will be used to verify quadratic calibration curves when analyzing WI compliance samples.'	Wisconsin requirement
Appendix B	Updated MDLs	Annual update

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs)

SOP NO.: LABENV-017.9

Original Information		
Prepared by:	Jennifer Nelson	Date: 01/27/94
Technical Review:	Sandra McDonald	Date: 12/12/94
QA/QC Coordinator:		Date:
Authorized by:	Cheryl Sykora	Date: 10/25/94

Revision Information		
Supersedes:	LABENV-017.8	Date: 04/28/09
Revised by:	Erin Sloan	Date: 04/23/09
Signature:	______________________	Date: __________
Technical Review:	Van Pham	Date: 04/23/09
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 04/27/09
Signature:	______________________	Date: __________

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Supersedes:	LABENV-017.8	Date: 04/28/09
Revised by:	Erin Sloan	Date:
Signature:	Erin A. Sloan	Date: 4/23/09
Technical Review:	Van Pham	Date:
Signature:	[signature]	Date: 4/23/09
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 4/27/09

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SOP TITLE: DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs)

1. PURPOSE

1.1 This document defines the procedure to be followed for the preparation and analysis for polychlorinated biphenyls (PCBs) in soil, wipe, and water by Gas Chromatography (GC) using an Electron Capture Detector (ECD). The SOP is applicable to samples typically analyzed by EPA 8082.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the SOP.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This method is applicable to wastewater, groundwater, soil, wipe, and solid samples.

3.2 Phthalate ester interferences may be removed through the use of sulfuric acid cleanup.

3.3 Elemental sulfur is readily extracted from samples and may cause chromatographic interferences. Sulfur can be removed through the use of copper powder cleanup.

3.4 The Sonication Method may be used when a sample has the potential to be detrimental to the ASE (tar samples, fine sediments, etc.).

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 A lab coat should be worn.

4.4 When working with organic compounds, wear safety glasses and solvent resistant gloves.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample’s integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Water samples should be collected in 1L amber glass bottles with Teflon lined caps and stored at 4 ± 2 °C.

5.4 The recommended holding time for water samples is 7 days until extraction and analysis within 40 days of extraction.

5.5 Soil samples should be collected in 4 oz. glass jars with Teflon lined caps and stored at 4 ± 2 °C.

5.6 The recommended holding time for soil samples is 14 days until extraction and analysis within 40 days of extraction.

5.7 Wipe samples should be received on 2" sterile gauze pads that are in 4 oz. glass jars with Teflon lined caps and stored at 4 ± 2 °C.

5.8 The recommended holding time for wipe samples is 1 year until extraction and analysis within 40 days of extraction.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 Gas chromatograph equipped with dual injectors, dual ECDs, and a data processing system

6.2 GC columns – Rtx®-CLPesticides™, 30 m x 0.32 mm, 0.5 µm film (Restek #11139), and Rtx®-CLPesticidesII™, 30 m x 0.32 mm, 0.25 µm film (Restek #11324) or equivalent. Whichever two columns are selected, they must be of dissimilar stationary phases.

6.3 Two liter Teflon separatory funnel, or equivalent

6.4 500 mL Kuderna Danish (K-D) flask

6.5 Steam bath

6.6 Orbital shaker

6.7 Accelerated Solvent Extractor (ASE) and associated parts and glassware

6.8 Turbo Vap II and associated parts and glassware

6.9 100 mm glass funnel

6.10 10 mL Kuderna Danish (K-D) concentrator

6.11 Graduated cylinder, 1000 mL

6.12 pH paper (0-14 Std. Units)

6.13 Disposable glass pasteur pipets and bulb

6.14 Volumetric flasks, 100 mL, 50 mL, 25 mL, 10 mL

6.15 Microliter syringes

6.16 Filter paper – Whatman 41, or equivalent

6.17 2” sterile gauze pads

6.18 Snyder column

6.19 Assorted laboratory glassware

6.20 Glass wool

6.21 PTFE solvent rinsed boiling beads, or equivalent

6.22 Disposable weighing aluminum dishes – prerinsed with hexane and methylene chloride

6.23 Disposable graduated pipets

6.24 2 mL autosampler vials

6.25 1 dram saver vials with Teflon liners

6.26 Kimwipes®, or equivalent

6.27 Hydromatrix® or equivalent – muffle at 400 °C for four hours before using

6.28 Ottawa Sand (20-30 mesh) or equivalent – muffle at 400 °C for four hours before using

6.29 Anhydrous Sodium Sulfate (Na_2SO_4) – muffle at 400 °C for four hours before using

6.30 Acetone – pesticide grade, or equivalent

6.31 Hexane – pesticide grade, or equivalent

6.32 Methylene Chloride (CH_2Cl_2) – pesticide grade, or equivalent

6.33 Organic free water

6.34 Sodium Hydroxide (NaOH) – reagent grade, or equivalent

6.35 Sulfuric Acid (H_2SO_4) – trace metal grade, or equivalent

6.36 Nitric Acid (HNO_3) – trace metal grade, or equivalent

6.37 10N Sodium Hydroxide – dissolve 40 g of the reagent grade NaOH in 100 mL organic free water

6.38 1:1 Sulfuric Acid – slowly add 100 mL of trace metal grade H_2SO_4 to 100 mL organic free water

6.39 1% Nitric Acid – add 1 part HNO_3 to 99 parts organic free water

6.40 Copper powder – (-10 + 40 mesh, Sigma-Aldrich #31,140-5) or equivalent

NOTE: Reactive copper is indicated by a bright, shiny appearance. If the copper is dull, wash with 1% HNO_3, rinse with organic free water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.

6.41 Extraction Solvent Mix for Solids – 3:1 Hexane and Acetone

6.42 Aroclor 1221 Stock – 1,000 µg/mL, Supelco #4-8098, or equivalent

6.43 Aroclor 1232 Stock – 1,000 µg/mL, Supelco #4-4805, or equivalent

6.44 Aroclor 1242 Stock – 1,000 µg/mL, Supelco #4-4806, or equivalent

6.45 Aroclor 1248 Stock – 1,000 µg/mL, Supelco #4-4807, or equivalent

6.46 Aroclor 1254 Stock – 1,000 µg/mL, Supelco #4-4808, or equivalent

6.47 Aroclor 1260 Stock – 1,000 µg/mL, Supelco #4-4809, or equivalent

6.48 Aroclor 1016-1260 Stock 1 – 1,000 µg/mL, Restek #32039, or equivalent

6.49 Aroclor 1016-1260 Stock 2 – 1,000 µg/mL, Ultra Scientific #PPM-8082 or equivalent, must be a different vendor or lot number than Aroclor 1016-1260 Stock 1 (used in PCB Second Source Standard)

6.50 Surrogate Stock – Restek #32000, 200 µg/mL for each of the following compounds: 2,4,5,6-Tetrachloro-m-xylene (TCMX), and Decachlorobiphenyl (DCB)

6.51 Surrogate Standard – dilute 0.25 mL of the Surrogate Stock Solution to 50 mL with 1:1 hexane and acetone to produce a 1.0 µg/mL Working Surrogate Standard. Store in a freezer for up to six months.

6.52 PCB Spike Standard – dilute 0.500 mL of the Aroclor 1260 Stock to 100 mL with 1:1 hexane and acetone to produce a 5.0 µg/mL PCB Spike Standard. Store in a freezer for up to six months.

6.53 Aroclor 1016-1260 Intermediate Solution – dilute 0.5 mL of the Aroclor 1016-1260 Stock 1 and 0.25 mL of the Surrogate Stock Solution to 10 mL with hexane to produce a 50 µg/mL Aroclor 1016-1260 and a 5.0 µg/mL Surrogate Standard. Store in a freezer for up to six months.

6.54 PCB Second Source Standard (CCAL/CCVS) – dilute 0.025 mL of the Aroclor 1016-1260 Stock 2 and 0.025 mL of the Surrogate Stock Solution to 25 mL with hexane to produce a 1.0 µg/mL Aroclor 1016-1260 and a 0.20 µg/mL Surrogate Second Source Standard. Store in a freezer for up to six months.

7. PROCEDURE

7.1 Preparation of Water Samples

7.1.1 Pre-rinse all glassware with extraction solvent.

7.1.2 Mark the water level on the outside of the bottle for later determination of volume.

7.1.3 Measure the pH of the sample and transfer to a pre-rinsed 2 L Separatory Funnel. (NOTE: If an evident layer of sediment is present, decant the sample and record on the extraction sheet.) The pH should be 5-9 su. If not, adjust the sample by using 10N NaOH or 1:1 H_2SO_4 and note on the extraction sheet.

7.1.4 Add 1.0 mL of 1.0 µg/mL Surrogate Standard to each sample, blank, and spike sample. Final concentration will be 1.0 µg/L.

7.1.5 For the samples in each analytical batch selected for spiking, add 1.0 mL of the 5.0 µg/mL PCB Spike Standard. Final concentration will be 5.0 µg/L. A typical batch will have an LCS and MS/MSD. LCS/LCSD will be substituted if enough sample is not provided.

7.1.6 Add 60 mL methylene chloride to the sample bottle and rinse. Transfer to the separatory funnel with the sample. (NOTE: If the sample was decanted, add 60 mL of methylene chloride directly to the separatory funnel.)

7.1.7 Cap and shake vigorously for 10 seconds and then vent. Cap and shake for 2 minutes. Allow the methylene chloride to separate from the sample.

7.1.7.1 If an emulsion interface between the layers is more than one-third the size of the solvent layer, the analyst should perform a beaker break without the use of Na_2SO_4.

7.1.7.2 Using a beaker, transfer the solvent layer into a glass 100 mm funnel containing a glass wool plug and about 2-3 inches of anhydrous muffled Na_2SO_4. Rinse the beaker with $MeCl_2$ and add to the funnel.

7.1.8 Drain into a 500 mL K-D flask equipped with a 10 mL K-D concentrator for Nitrogen Blowdown.

7.1.9 Repeat steps above with two additional fresh portions of methylene chloride.

7.1.10 After the final extraction, rinse the sodium sulfate with 20-30 mL of methylene chloride to complete the quantitative transfer.

7.1.11 If the emulsion layer is still present after the final shake, the analyst should employ mechanical techniques to complete the phase separation. Refer to the protocol found in Work Instruction (WI) 'Handling Emulsions'

7.1.12 Fill sample bottle with tap water to mark made previously. Transfer to a 1000 mL graduated cylinder and record volume on extraction sheet

7.1.13 K-D Technique / Nitrogen Blowdown

7.1.13.1 Add one solvent rinsed boiling bead to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-85 ºC) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot vapor. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 20 mL, add approximately 20 mL of hexane through the Snyder column.

7.1.13.2 Concentrate to approximately 5 mL, remove the K-D apparatus from the steam bath, and allow it to cool. Remove the Snyder column.

7.1.13.3 Put the concentrator tube in a warm bath (about 35 °C) and evaporate the solvent volume to less than 5 mL using a gentle stream of clean, dry nitrogen. During evaporation, the tube solvent level must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Do not allow the extract to go dry. Using a disposable pipet, adjust the final volume to 5.0 mL with hexane and mix the extract completely.

7.1.13.4 Transfer approximately 1 mL to a 2 mL autosampler vial and put the rest in a 4 mL saver vial. Store in freezer until analysis.

7.2 Preparation of Soil Samples – ASE technique

7.2.1 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

7.2.2 Place two filters on top of the open end of the cell body. Use the black cylindrical insertion tool to push filter to the bottom of the assembled cell body. Very fine soils may require three filters.

7.2.3 Use a 1:1 Ottawa Sand:Hydromatrix® mixture for the blank and Laboratory Control Sample (LCS). A typical batch will have an LCS and MS/MSD. LCS/LCSD will be substituted if enough sample is not provided.

7.2.4 Weigh approximately 15 g of sample into a prerinsed disposable aluminum dish. Record the weight to the nearest 0.01 g.

7.2.5 Mix the sample with Hydromatrix®, or equivalent, using approximately a 1:1 ratio by volume, until free-flowing. Depending on the matrix, the amount of sample may need to be reduced.

7.2.6 Place the extraction cell funnel on open end of cell body. Load sample into cell through funnel. Gently tap cell on hard surface to pack sample evenly and to reduce void volume.

7.2.7 All samples should come within 1 cm of the top of the vessel. If a sample does not, use sand to fill.

7.2.8 When the transfer is complete, remove the funnel. Add 1.0 mL of 1.0 µg/mL Surrogate Standard to each sample, blank, and spike sample. Final concentration will be 0.067 mg/kg.

7.2.9 For the samples in each analytical batch selected for spiking, add 1.0 mL of the 5.0 µg/mL PCB Spike Standard. Final concentration will be 0.33 mg/kg.

7.2.10 Place filter paper on top of the sample. Remove any debris from cell threads and screw the second end cap onto open end of the cell body, and tighten.

7.2.11 Place completed extraction cell into position #1 on ASE. Place the corresponding collection vial into position #1 below.

7.2.12 Repeat steps above for additional samples.

7.2.13 Fill solvent bottles with the 3:1 Hexane to Acetone Extraction Solvent Mix.

7.2.14 Make sure pressure on gas tank is set to 180 psi. Make sure that solvent bottle pressure is 10 psi, system air pressure is 50 psi, and compression oven pressure is 130 psi.

7.2.15 Refer to Equipment SOP entitled 'ASE' for equipment set-up and operation.

7.2.16 Attach a K-D concentrator to a 500 mL evaporation flask for Nitrogen Blowdown or a 200 mL Turbo Vap II concentration vial.

7.2.17 Decant extraction solvent from the ASE collection vial through a hexane rinsed funnel with sodium sulfate and glass wool. Rinse the collection vial three times to complete quantitative transfer. Collect the extract in the assembled K-D concentrator flask or a 200 mL Turbo Vap II concentration vial.

7.2.18 K-D Technique / Nitrogen Blowdown

7.2.18.1 Add one solvent rinsed boiling bead to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of hexane to the top of the column. Place the K-D apparatus on a hot water bath (90-95 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot vapor. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

7.2.18.2 When the apparent volume of liquid reaches 5 mL, remove the K-D apparatus from the water bath and allow it to cool. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane.

7.2.18.3 Put the concentrator tube in a warm bath (about 35 ºC) and evaporate the solvent volume to less than 5 mL using a gentle stream of clean, dry nitrogen. During evaporation, the tube solvent level must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Do not allow the extract to go dry. Using a disposable pipet, adjust the final volume to 5.0 mL with hexane and mix the extract completely.

7.2.18.4 Transfer approximately 1 mL to a 2 mL autosampler vial and put the rest in a 4 mL saver vial. Store in freezer until analysis.

7.2.19 Turbo Vap II

7.2.19.1 Place the Turbo Vap collection tube in the Turbo Vap.

7.2.19.2 Set the water bath temperature to 40 °C and the pressure to 8-12 psi.

7.2.19.3 Set the Turbo Vap to monitor by 'sensor' to achieve a final volume of approximately 4 mL.

7.2.19.4 Using a disposable pipet, adjust the final volume to 5.0 mL with hexane and mix the extract completely. Transfer approximately 1 mL to a 2 mL autosampler vial and the remaining extract to a 4 mL saver vial. Store in freezer until analysis.

7.3 Preparation of Wipe Samples

7.3.1 For QC samples, label three 4 oz. jars for the Blank, LCS, and LCSD and add one 2" sterile gauze pad to each jar.

7.3.2 Add 1.0 mL of 1.0 µg/mL Surrogate Standard to each sample, blank, and spike sample. Final concentration will be 1.0 µg/wipe.

7.3.3 For the samples in each analytical batch selected for spiking, add 1.0 mL of the 5.0 µg/mL PCB Spike Standard. Final concentration will be 5.0 µg/wipe. A typical batch will have an LCS/LCSD.

7.3.4 Add 25 mL of hexane to all QC and sample jars.

7.3.5 Place on the orbital shaker for 20 minutes.

7.3.6 Remove solvent with a glass disposable pipet and quantitatively transfer into a prerinsed glass funnel containing a filter paper and sitting atop a 500 mL K-D flask equipped with a 10 mL K-D concentrator for Nitrogen Blowdown or a 200 mL Turbo Vap II concentration vial.

7.3.7 K-D Technique / Nitrogen Blowdown

7.3.7.1 Add one solvent rinsed boiling bead to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of hexane to the top of the column. Place the K-D apparatus on a hot water bath (90-95 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot vapor. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane.

7.3.7.2 Put the concentrator tube in a warm bath (about 35 °C) and evaporate the solvent volume to less than 5 mL using a gentle stream of clean, dry nitrogen. During evaporation, the tube solvent level must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Do not allow the extract to go dry. Using a disposable pipet, adjust the final volume to 5.0 mL with hexane and mix the extract completely.

7.3.7.3 Transfer approximately 1 mL to a 2 mL autosampler vial and put the rest in a 4 mLsaver vial. Store in freezer until analysis.

7.3.8 Turbo Vap II

7.3.8.1 Place the Turbo Vap collection tube in the Turbo Vap.

7.3.8.2 Set the water bath temperature to 40 °C and the pressure to 8-12 psi.

7.3.8.3 Set the Turbo Vap to monitor by 'sensor' to achieve a final volume of approximately 4 mL.

7.3.8.4 Using a disposable pipet, adjust the final volume to 5.0 mL with hexane and mix the extract completely. Transfer approximately 1 mL to a 2 mL autosampler vial and the remaining extract to a 4 mL saver vial. Store in freezer until analysis.

7.4 Calibration

7.4.1 Prepare working standards at a minimum of 5 concentration levels, ranging from 0.4-3.0 µg/mL, by diluting the 50 µg/mL / 5.0 µg/mL Aroclor 1016-1260 Intermediate Solution with hexane. A typical calibration curve would be:

Inter. Solution (mL/25 mL)	Aroclor Conc. (µg/mL)	Surrogate Conc. (µg/mL)
0.2	0.40	0.040
0.3	0.60	0.060
0.4	0.80	0.080
0.5	1.0	0.10
1.0	2.0	0.20
1.5	3.0	0.30

7.4.2 When selecting peaks for quantitation, choose 5-7 peaks that are at least 25% of the height of the largest Aroclor peak. Assign the concentration to each peak. Concentrations in the standard are determined using the mean value resulting from these peaks.

7.4.3 The average response factor should be calculated for each compound. The percent relative standard deviation (%RSD) should be less than 20% for each compound. If the %RSD of any compound is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

7.4.4 If the %RSD of any compound is greater than 20%, construct calibration curves of area versus concentration using a first order or linear fit. Correlation coefficients (r) should be 0.990 or greater.

7.4.5 Calibration curve calculations are found in the QA Manual.

7.4.6 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.4.7 Use the PCB Second Source Standard as the continuing calibration standard – CCAL/CCVS.

7.4.8 Stock Standards should be stored in a freezer and replaced following manufacturer's expiration date or one year after opening, whichever comes first. Working standards should be stored in a freezer and replaced every 6 months or when analysis of continuing calibration standards indicate degradation or loss.

7.4.9 The RLVs of the other 5 Aroclors are used for pattern recognition. These standards may also be used as a single point calibration if the 1016-1260 is being used for the 5-point calibration and the Aroclor result is within 20% of the applicable RLV. An Aroclor standard may be analyzed to quantitate a sample run in the previous 12 hours.

NOTE: If a sample is expected to contain a specific Aroclor, the analyst may do a minimum 5-point calibration of that Aroclor in place of the 1016-1260. Prepare a calibration curve for the Aroclor of interest.

7.4.10 If a sample contains an Aroclor with an on-column concentration estimated to be between the reporting limit and 1.0 µg/mL, a 1.0 µg/mL standard is available to run as a dilution or as the single point calibration standard. For samples containing estimated on-column concentrations above 1.0 µg/mL, the sample is diluted so that the 1.0 µg/mL standard can be used. With a single point calibration, the sample should be within ± 20% of the concentration of the single-point standard to maximize accuracy.

7.5 Analysis

7.5.1 GC Conditions

7.5.1.1 Columns: Rtx®-CLPesticides™, 30m x 0.32mm, 0.5 µm film (Restek #11139), and Rtx®-CLPesticidesII™, 30 m x 0.32 mm, 0.25 µm film (Restek #11324) or equivalent

7.5.1.2 Injector Temperature: 250 °C

7.5.1.3 Detector Temperature: 310 °C

7.5.1.4 ECD 1 Temp Program: 150 °C for 0.5 min, 10 °C/min ramp to 200 °C, 5.0 °C/min ramp to 310 °C

7.5.1.5 ECD 2 Temp Program: 175 °C for 0 min, 6 °C/min ramp to 300 °C

7.5.1.6 Flow Rate: 1.6 mL/min (ECD 1), 1.0 mL/min (ECD 2); Constant Flow

7.5.1.7 Split Ratio: 40:1 (ECD 1), 60:1 (ECD 2)

7.5.1.8 GC Range: 0

7.5.1.9 Attenuation: 0

7.5.1.10 Injection Volume: 1.0 µL

7.5.2 The 1016-1260 mix may be used to demonstrate that a sample does not contain peaks that represent any Aroclor. As such, it is not necessary to run standards for each of the other 5 Aroclors, but it may be practical.

7.5.3 It is appropriate to perform an area sum on a sample in which the Aroclor pattern is no longer recognizable due to environmental factors. The same integration technique must be performed on standards. Any peaks in the area sum window not identifiable as PCBs on the basis of retention times should be subtracted from the total area. This procedure must be thoroughly documented and described to the data user.

7.5.4 Analyze the PCB Second Source Standard (CCAL/CCVS) at the beginning of each sequence, every 12 hours thereafter and at the end of the sequence. Recoveries should be ± 15% or corrective action should be taken. Corrective action may include reinjection, making a new standard, maintenance, and/or flagging the data.

7.5.5 If the response for a peak exceeds the working range of the system or the highest standard, dilute the extract with hexane and re-analyze.

7.5.6 If the presence of phthalate esters or other interfering compounds are suspected or found, a sulfuric acid cleanup may be performed.

7.5.6.1 Pipet 1.5 – 2 mL of 1:1 H_2SO_4 and 1.5 – 2 mL of extract into a clear glass 5 mL vial.

7.5.6.2 Shake vigorously for two minutes.

7.5.6.3 If a clear separation is not visible between the acid and solvent, centrifuge for 3-5 minutes.

7.5.6.4 If the acid (bottom) layer is colored, repeat steps above until the acid layer is colorless.

7.5.6.5 Remove the solvent (top) layer, place in an autosampler vial, and proceed with the analysis.

7.5.7 If the presence of sulfur is suspected or found, a copper powder cleanup may be performed.

7.5.7.1 To the autosampler vial containing 1 mL of extract, add approximately 2 g of reactive copper powder.

7.5.7.2 Shake vigorously for two minutes; allow to settle.

7.5.7.3 Remove the solvent layer, place in an autosampler vial, and proceed with the analysis.

7.5.7.4 Do not reuse the extract containing the copper powder.

7.6 Calculation

7.6.1 Identify the Aroclor type. For all samples that contain multiple Aroclors, calculate each Aroclor separately. Pattern recognition and experience of the analyst is a major factor in Aroclor identification.

7.6.2 Calculate the concentration of the Aroclor in the sample using one of the following equations:

$$Water\ Concentration\ (\mu g / L) = \frac{(C_{ex})(V_{ex})(F)}{V_o}$$

$$Soil\ Concentration\ (mg / kg) = \frac{(C_{ex})(V_{ex})(F)}{(W)(D)}$$

$$\text{Wipe Concentration } (\mu g / wipe) = (C_{ex})(V_{ex})(F)$$

C_{ex} = extract concentration, µg/mL
V_{ex} = extract volume, mL
F = dilution factor (diluted volume/extract volume)
V_o = volume of sample extracted, L
W = sample weight, g
D = % dry weight of sample/100, or 1 for wet weight basis

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

8.2 Highly contaminated samples are returned to the client for disposal.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, when there is a change in the test method that may affect how the test is performed or when there is a major change in instrumentation. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. The method blank must be less than the reporting limit or the sample batch is re-extracted if possible. If it is not possible to re-extract, the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Accuracy control limits are set at 70.0-130% for LCS and MS. Surrogate limits are generated semi-annually, using 20 Percent Recovery points, as follows:

9.3.1.1 Upper and Lower Control Limit = Mean ± 3s

9.3.1.2 Upper and Lower Warning Limit = Mean ± 2s

9.3.1.3 s = Standard deviation

9.3.1.4 For Arizona compliance, the surrogate lower control limit can not calculate below the lowest standard on the calibration curve (e.g. lowest standard = 0.04 µg/mL, spike is at 0.2 µg/mL, % can not be below 20.0%). The Minnesota Pollution Control Agency sets a guideline that the lower control limit can not be < 30.0%. For consistency between methods 608, 8081A, and 8082, LEGEND will use 40.0% (8081A limit).

9.3.2 Precision control limits are set at 20.0% RPD for LCS/LCSD and generated for MS/MSD. In-house control charts are generated semi-annually, using 20 RPD points, as follows:

9.3.2.1 Control Limit = Mean + 3s

9.3.2.2 Warning Limit = Mean + 2s

9.3.2.3 s = Standard deviation

9.3.2.4 RPD = Relative Percent Difference

9.3.3 QC calculations are found in the QA Manual

9.3.4 LCS, MS and surrogates are reviewed.

9.3.5 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is re-extracted and/or re-analyzed if possible. If the batch cannot be re-analyzed, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.6 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS is flagged and/or a case narrative is written.

9.3.7 If a sample surrogate is outside the limits, the sample is re-extracted and/or reanalyzed if possible. If the sample cannot be reanalyzed, the data is flagged next to the actual result in the report.

10. REPORTING

10.1 Soil sample results are reported in mg/kg on a dry weight basis.

10.2 Water sample results are reported in µg/L.

10.3 Wipe sample results are reported in µg/wipe and as a Modified EPA 8082.

10.4 The reported result is rounded to two significant figures.

10.5 The results are placed in the client file and a report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

12. REFERENCES

12.1 EPA Methods 3510C, 3545, 3660B, 3665A, 8082, 8000B (MN), 8000C (AZ)

Appendix A

Initial Demonstration of Capability (IDC)
Polychlorinated Biphenyls (PCBs)

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards of all the aroclors in Ottawa sand and/or lab-grade water and a reagent blank. Only the 1260 Aroclor is analyzed for the wipe IDC.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: 70.0-130%
   Precision: ≤ 20% RPD

   If the standards were not extracted, the results must meet the following criteria:

   Accuracy: 85.0-115%
   Precision: ≤ 20% RPD

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the QA/QC Coordinator signs the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

10. For the analysis IDC all aroclors must be analyzed. Only one aroclor is required for the extraction IDC.

11. A minimum of two blind standards containing different aroclors must be analyzed to demonstrate aroclor pattern identification for the analysis IDC unless the analyst has already satisfied this requirement by another PCB method.

Appendix B

Method Detection Limits and Reporting Limits
Polychlorinated Biphenyls (PCBs)

Parameter	Water MDL (µg/L)	Water RL (µg/L)	Soil MDL (mg/kg)	Soil RL (mg/kg)	Wipe MDL (µg/wipe)	Wipe RL (µg/wipe)
Aroclor 1016	0.19	2.0	0.012	0.20	0.46	2.0
Aroclor 1221	0.22	2.0	0.020	0.20	-----	2.0
Aroclor 1232	0.21	2.0	0.015	0.20	-----	2.0
Aroclor 1242	0.34	2.0	0.019	0.20	-----	2.0
Aroclor 1248	0.53	2.0	0.011	0.20	-----	2.0
Aroclor 1254	0.19	2.0	0.015	0.20	-----	2.0
Aroclor 1260	0.19	2.0	0.011	0.20	0.42	2.0

DOCUMENT REVIEW

DOCUMENT:	SOP LABENV-017.9
REVIEWER:	Erin Sloan
DATE:	03/19/09

SECTION	**CHANGE**	**RATIONALE**
3.4	Added subsection	To match Pesticide SOP LABENV-025.6
5.7	Changed “2-oz” to “4-oz”	Legend supplies 4-oz jars to clients
7.4.9	Deleted, “Standards of the other five Aroclors are needed for pattern recognition” Added, “The RLVs of the other five Aroclors are used for pattern recognition” Added “…and the Aroclor result is within 20% of the applicable RLV”.	Clarification of what can be used for pattern recognition per EPA 8082
7.4.10	Added, “with an on-column concentration estimated to be between the reporting limit and 1.0 µg/mL, a 1.0 µg/mL standard is available to run as a dilution or as the single point calibration standard. For samples containing estimated on-column concentrations above 1.0 µg/mL, the sample is diluted so that the 1.0 µg/mL standard can be used. With a single point calibration…”	Clarification of single point calibration.
Appendix B	Updated MDLs	Annual update

UMP006527

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF GASOLINE RANGE ORGANICS (GRO) AND PETROLEUM VOLATILE ORGANIC COMPOUNDS (PVOC)

SOP NO.: LABENV-010.5

Original Information		
Prepared by:	Chris Bremer	Date: 07/28/92
Technical Review:		Date:
QA/QC Coordinator:	Corrine Goodrich	Date: 08/05/92
Authorized by:	Cheryl Sykora	Date: 07/28/92

Revision Information		
Supersedes:	LABENV-010.4	Date: 04/02/08
Revised by:	Yen Pham	Date: 03/17/09
Signature:	______________________	Date: __________
Technical Review:	Sonny Hang	Date: 03/17/09
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 03/17/09
Signature:	______________________	Date: __________

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Supersedes:	LABENV-010.4	Date: 04/02/08
Revised by:	Yen Pham	Date:
Signature:	Yenpham	Date: 3/17/09
Technical Review:	Sonny Hang	Date:
Signature:	[signature]	Date: 3/17/09
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 3/17/09

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FORM GEN-021 (05/07)

SOP TITLE: DETERMINATION OF GASOLINE RANGE ORGANICS (GRO) AND PETROLEUM VOLATILE ORGANIC COMPOUNDS (PVOC)

1. PURPOSE

1.1 This document defines the procedure used to determine gas range organics (GRO), petroleum volatile organic compounds (PVOC), and total petroleum hydrocarbons as gasoline (TPH-Gas) in water and soil samples by purge and trap-gas chromatography (GC) with photoionization and flame ionization detectors (PID and FID) in series. The SOP is applicable to samples typically analyzed by Wisconsin DNR Modified GRO Method PUBL-SW-140 and EPA Methods 8000B and 8015B.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the standard operating procedure.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) in purge and trap techniques shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This procedure is limited to wastewater, groundwater, and solid samples.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 A lab coat and safety glasses should be worn.

4.4 When working with organic compounds, wear solvent resistant gloves.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample’s integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample’s integrity.

5.3 Water samples should be collected in triplicate in 40 mL VOC vials preserved with 0.5 mL of 1:1 HCl. Samples should be collected without agitation or headspace and stored at 4 ± 2 °C. A trip blank comprised of organic free water, also preserved, should accompany the samples.

5.4 For WI GRO/PVOC soil samples, 10 g of soil should be collected in a tared 40 mL VOA vial containing 10 mL of purge and trap grade methanol and stored at 4 ± 2 °C. A methanol trip blank should accompany the samples.

5.5 The recommended holding times from collection until analysis are 21 days for preserved soil samples and 14 days for preserved water samples. The holding time for unpreserved water samples is 7 days.

5.6 For method EPA 8015B (TPH as Gasoline), soil samples may be collected in either tared 40 mL VOA vials containing 10 mL of purge and trap grade methanol or jars with zero headspace. The recommended holding time for TPH-Gas soil and preserved water samples is 14 days from collection until analysis.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 GC equipped with PID/FID in series

6.2 Purge and trap autosampler and concentrator

6.3 Column – DB5-length 30 m, ID 0.53, or equivalent

6.4 OI 4560 Concentrator Trap – OI Analytical BTEX J, or equivalent

6.5 Encon Concentrator Trap – EST modified BTEX M, or equivalent

6.6 Balance, capable of reading 0.01 g

6.7 Ultrasonic bath

6.8 2 oz Amber jars with Teflon lined caps

6.9 40 mL VOC vials with Teflon lined caps

6.10 20 mL VOC vials with Teflon lined caps

6.11 5 mL Luerlock syringe

6.12 Assorted volumetric flasks

6.13 Assorted microliter syringes

6.14 Stainless steel spatula

6.15 Organic free water

6.16 Methanol – purge and trap grade, or equivalent

6.17 GRO/PVOC free sand or soil, oven dried at $\geq$ 100 ºC for a minimum of one hour

6.18 GRO/PVOC Stock Solution – 10,000 µg/mL GRO/1,000 µg/mL each PVOC compound, Ultra # UST-100, or equivalent

6.19 GRO/PVOC Second Source Stock Solution – 10,000 µg/mL GRO/1,000 µg/mL each PVOC compound, Absolute # 90379, or equivalent, must be a different manufacturer or at least different lot number than stock used in the calibration curve

6.20 TPH as Gasoline Stock – 20,000 µg/mL Gasoline, Absolute Standards, Inc. # 51010 or equivalent

6.21 Surrogate Stock – 2,000 µg/mL, 1-chloro-4-fluorobenzene, Absolute Standards, Inc. # 60013, or equivalent

6.22 MPM-16 GRO/PVOC Calibration Solution 1 – dilute 50 µL of the 10,000/1,000 µg/mL GRO/PVOC Stock Solution and 25 µL of the 2,000 µg/mL Surrogate Stock to 10 mL with methanol to produce an MPM-16 50/5 µg/mL GRO/PVOC / 5 µg/mL Calibration Solution 1

6.23 MPM-16 GRO/PVOC Calibration Solution 2 – dilute 100 µL of the MPM-16 50/5 µg/mL GRO/PVOC / 5 µg/mL Calibration Solution 1 to 1 mL with methanol to produce an MPM-16 5/0.5 µg/mL GRO/PVOC (only the PVOC is used) / 0.5 µg/mL Calibration Solution 2

6.24 EST/Archon GRO/PVOC Calibration Solution 1 – dilute 50 µL of the 10,000/1,000 µg/mL GRO/PVOC Stock Solution and 25 µL of the 2,000 µg/mL Surrogate Stock to 1.0 mL with methanol to produce an EST/Archon 500/50 µg/mL GRO/PVOC / 50 µg/mL Calibration Solution 1

6.25 EST/Archon GRO/PVOC Calibration Solution 2 – dilute 100 µL of the EST/Archon 500/50 µg/mL GRO/PVOC/ 50 µg/mL Calibration Solution 1 to 1 mL with methanol to produce a EST/Archon 50/5 µg/mL GRO/PVOC (only the PVOC is used) / 5 µg/mL Calibration Solution 2

6.26 MPM-16 TPH as Gasoline Calibration Solution / Spike Standard – dilute 25 µL of the 20,000 µg/mL TPH as Gasoline Stock to 10 mL with methanol to produce an MPM-16 50 µg/mL TPH as Gasoline Calibration Solution / Spike Standard

6.27 EST/Archon TPH as Gasoline Calibration Solution / Spike Standard – dilute 200 µL of the 20,000 µg/mL TPH as Gasoline Stock to 10 mL with methanol to produce an EST/Archon 400 µg/mL TPH as Gasoline Calibration Solution / Spike Standard

6.28 MPM-16 GRO/PVOC Calibration Verification Intermediate (CVI) / Water Spike Standard – dilute 200 µL of the 10,000/1,000 µg/mL GRO/PVOC Stock Solution to 10 mL with methanol to produce an MPM-16 200/20 µg/mL GRO/PVOC CVI / Water Spike Standard

6.29 MPM-16 GRO/PVOC Second Source Calibration Verification Standard – dilute 200 µL of the 10,000/1,000 µg/mL GRO/PVOC Second Source Stock Solution to 10 mL with methanol to produce an MPM-16 200/20 µg/mL GRO/PVOC Second Source Calibration Verification Standard

6.30 EST/Archon GRO/PVOC Calibration Verification Intermediate (CVI) / Water Spike Standard – dilute 100 µL of the 10,000/1,000 µg/mL GRO/PVOC Stock Solution to 1.0 mL with methanol to produce an EST/Archon 1,000/100 µg/mL GRO/PVOC CVI / Water Spike Standard

6.31 EST/Archon GRO/PVOC Second Source Calibration Verification Standard – dilute 100 µL of the 10,000/1,000 µg/mL GRO/PVOC Second Source Stock Solution to 1.0 mL with methanol to produce an EST/Archon 1,000/100 µg/mL GRO/PVOC Second Source Calibration Verification Standard

6.32 GRO/PVOC Soil Spike Standard – weigh 25 g of clean sand or soil into a 2 ounce wide mouth jar and add 25 mL of methanol and 125 µL of the 10,000/1,000 µg/mL GRO/PVOC Stock Solution to produce a 50/5 µg/mL GRO/PVOC Soil Spike to be used for both autosampler styles; store in the freezer

6.33 MPM-16 Surrogate Standard – dilute 125 µL of the 2,000 µg/mL Surrogate Stock to 10 mL with methanol to produce a MPM-16 25 µg/mL Surrogate Standard

6.34 EST/Archon Surrogate Standard – dilute 312.5 µL of the 2,000 µg/mL Surrogate Stock to 5 mL with methanol to produce an EST/Archon 125 µg/mL Surrogate Standard which is stored in the Archon pressurized by He

NOTE: Store stock solutions with minimal headspace in a refrigerator. Once opened, stocks must be replaced after 6 months or sooner if comparison with check standards indicates a problem. Prepared solutions and standards should be replaced after a maximum of one month or sooner if degradation is apparent.

7. PROCEDURE

7.1 Calibration

7.1.1 Prepare GRO/PVOC working standards at a minimum of 5 concentration levels, ranging from 0.5-300 µg/L (PVOC) and 50-3000 µg/L (GRO), by diluting the appropriate concentrator GRO/PVOC Calibration Solutions with reagent water. Typical calibration curves (ICAL) would be:

MPM-16

5/0.5 µg/mL GRO/PVOC µL/5 mL	50/5 µg/mL GRO/PVOC µL/5 mL	GRO Conc. (µg/L)	PVOC/ Surrogate Conc. (µg/L)
5.0	---	---	0.50
10	---	---	1.0
---	5.0	50	5.0
---	10	100	10
---	50	500	50
---	100	1000	100
---	200	2000	200
---	300	3000	300

EST/Archon

50/5.0 µg/mL GRO/PVOC µL/40 mL	500/50 µg/mL GRO/PVOC µL/40 mL	GRO Conc. (µg/L)	PVOC/ Surrogate Conc. (µg/L)
4.0	---	---	0.50
8.0	---	---	1.0
---	4.0	50	5.0
---	8.0	100	10
---	40	500	50
---	80	1000	100
---	160	2000	200
---	240	3000	300

7.1.2 Prepare TPH as Gasoline working standards at a minimum of 5 concentration levels, ranging from 50-3000 µg/L by diluting the appropriate concentrator TPH as Gasoline Calibration Solution with reagent water. Typical calibration curves (ICAL) would be:

MPM-16

50 µg/mL TPH as Gas µL/5 mL	TPH as Gas Concentration (µg/L)
5.0	50
10	100
50	500
100	1000
150	1500
200	2000
300	3000

EST/Archon

400 µg/mL TPH as Gas µL/40 mL	TPH as Gas Concentration (µg/L)
5.0	50
10	100
50	500
100	1000
150	1500
200	2000
300	3000

NOTE: Surrogates for the TPH as Gasoline analysis are calculated using the GRO/PVOC surrogate curve.

7.1.3 Prepare GRO or TPH as Gasoline calibration curves of Concentration vs. Response using linear regression. The correlation coefficient (r) of the calibration curves must be at least 0.990.

7.1.4 Prepare individual PVOC calibration curves of Concentration vs. Response using average response factor. If the %RSD of any compound is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation. If the %RSD of any compound is greater than 20%, construct calibration curves of area versus concentration using a first order or linear fit. Correlation coefficients (r) should be 0.990 or greater.

7.1.4.1 For naphthalene in water and soil, do not include the 0.50 and 1.0 µg/L levels.

7.1.4.2 For MTBE, do not include the 0.50, 1.0, and 300 µg/L levels for water samples and do not include the 300 µg/L levels for soil samples.

7.1.5 Calibration curve calculations are found in the QA Manual.

7.1.6 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.1.7 Verify the GRO/PVOC calibration curve by running the appropriate Second Source Calibration Verification Standard.

7.1.7.1 For the MPM-16, add 25 µL of the MPM-16 200/20 µg/mL GRO/PVOC Second Source Calibration Verification Standard and 5 µL of the MPM-16 25 µg/mL Surrogate Standard to the syringe. Final concentration for the GRO/PVOC Second Source Calibration Verification Standard will be 1000/100 µg/L GRO/PVOC and final concentration for the surrogate will be 25 µg/L (based on a 5 mL volume). Recoveries for the GRO/PVOC Second Source Calibration Verification Standard should be ± 20% or corrective action should be taken.

7.1.7.2 For the EST/Archon, add 40 µL of the EST/Archon 1,000/100 µg/mL GRO/PVOC Second Source Calibration Verification Standard to the 40 mL vial. Program the Archon to add 1 µL of the EST/Archon 125 µg/mL Surrogate Standard to the 5 mL aliquot being analyzed. Final concentration for the GRO/PVOC Second Source Calibration Verification Standard will be 1,000/100 µg/L GRO/PVOC (based on a 40 mL volume) and final concentration for the surrogate will be 25 µg/L (based on a 5 mL volume). Recoveries for the GRO/PVOC Second Source Calibration Verification Standard should be ± 20% or corrective action should be taken.

7.1.7.3 Corrective action may include reinjection, maintenance, flagging the data, and/or preparing a new initial calibration curve.

7.1.8 If the sample concentration exceeds the initial calibration range, dilute the sample and reanalyze.

7.2 Analysis

7.2.1 GC Conditions

7.2.1.1 Initial temperature: 35 °C

7.2.1.2 Initial time: 5 min

7.2.1.3 Ramp rate: 5 °C/min to 105 °C

7.2.1.4 Hold: 0 min

7.2.1.5 Second ramp rate: 20 °C/min to 250 °C final temperature

7.2.1.6 Column flow-

7.2.1.6.1 Hydrogen gas: approximately 40 mL/min

7.2.1.6.2 Helium makeup gas: approximately 30 mL/min

7.2.1.6.3 Helium carrier gas: approximately 6 mL/min

7.2.1.6.4 Air: approximately 160 mL/min

7.2.1.6.5 Detector Temperature: 275 °C

7.2.1.6.6 Injector Temperature: 250 °C

7.2.2 Purge and Trap Conditions

7.2.2.1 Purge flow: approximately 40 mL/min

7.2.2.2 Purge time: 11 min

7.2.2.3 Desorb pre-heat temperature: 250 °C (Encon only)

7.2.2.4 Desorb temperature: 250 °C

7.2.2.5 Desorb time: 1 min. (Encon), 6 min. (OI 4560)

7.2.2.6 Bake: 260 °C for 15 min

7.2.2.7 6 port valve: 120 °C

7.2.2.8 Transfer line: 120 °C

7.2.2.9 Auto sampler valve & transfer line: 120 °C

7.2.2.10 OI 4560 Water MGMT on: 150 °C during purge, 50 °C desorb, 240 °C bake

7.2.2.11 Encon MORT 40 °C purge and desorb, 260 °C bake

7.2.3 Typical Water Batch

GRO/PVOC
CVS/LCS – GRO/PVOC
Method blank
20 samples
Sample duplicate
MS – PVOC (GRO MS is not quantitated per the method)
LCSD – GRO/PVOC

TPH as Gas/BTEX
CVS/LCS – TPH as Gas
CVS/LCS – BTEX
Method blank
20 samples
Sample duplicate
MS – BTEX
LCSD – BTEX
LCSD – TPH as Gas

TPH as Gas
CVS/LCS –TPH as Gas
Method blank
20 samples
Sample duplicate
MS – TPH as Gas
LCSD – TPH as Gas

7.2.3.1 Station blanks and additional autosampler blanks do not count as samples.

7.2.3.2 Dilutions and reruns performed in the same sequence count as one sample.

7.2.3.3 The CVS/LCS is analyzed at the beginning of the run (if an initial calibration curve was not analyzed).

7.2.4 OI 4650 MPM-16 Water Sample Analysis

7.2.4.1 Remove the plunger from a 5 mL syringe.

7.2.4.2 Pour reagent water into the syringe barrel.

7.2.4.3 Attach the plunger and compress the reagent water.

7.2.4.4 Adjust the reagent water volume to 5.0 mL.

7.2.4.5 For the water GRO/PVOC CVS/LCS, add 25 µL of the MPM-16 200/20 µg/mL GRO/PVOC CVI / Water Spike Standard and 5 µL of the MPM-16 25 µg/mL Surrogate Standard to the syringe. Final concentration for the GRO/PVOC CVS/LCS will be 1000/100 µg/L GRO/PVOC and final concentration for the surrogate will be 25 µg/L (based on a 5 mL volume).

7.2.4.6 For the TPH as Gas CVS/LCS, add 100 µL of the MPM-16 50 µg/mL TPH as Gasoline Calibration Solution / Spike Standard to the syringe. Final concentration for the TPH as Gasoline CVS/LCS will be 1,000 µg/L (based on a 5 mL volume).

7.2.4.7 Recoveries for the GRO/PVOC CVS/LCS should be ± 20%, the TPH as Gasoline CVS/LCS should be ± 15% or corrective action should be taken. Examples of corrective action may include inspecting the system for leaks, checking for errors in standard preparation or degradation of the standard mix, or evaluating the chromatography system. If major corrective action is required, such as cleaning the detector, lamp, jet or replacing the chromatographic column, a new initial calibration would need to be generated before samples could be analyzed.

7.2.4.8 A method blank is set up per the instructions above without the addition of the CVI. For WI GRO analysis, the method blank must be less than 50 µg/L GRO or the sample batch is re-analyzed if possible. If it is not possible to re-analyze, the data will be flagged where appropriate.

7.2.4.9 Allow all samples to come to ambient temperature.

7.2.4.10 Pour a sample into the syringe barrel. Run one sample in duplicate.

7.2.4.11 Attach the plunger and compress the sample.

7.2.4.12 Adjust the sample volume to 5.0 mL. If there is only one sample vial, pour the remaining sample into a 20 mL VOC vial as a backup in case reruns are necessary. Removal of the sample aliquot destroys the validity of that sample vial for future analyses.

7.2.4.13 Add 5 µL of the MPM-16 25 µg/mL Surrogate Standard to each blank, sample, and QC. Final concentration will be 25 µg/L (based on a 5 mL volume).

7.2.4.14 For the samples in each analytical batch selected for spiking, add 25 µL of the MPM-16 200/20 µg/mL GRO/PVOC Water Spike Standard to the syringe. Final concentration will be 1,000/100 µg/L GRO/PVOC (based on a 5 mL volume). If a batch is analyzed for only TPH as Gas, analyze a TPH matrix spike by adding 100 µL of the MPM-16 50 µg/mL TPH as Gasoline Spike Standard to the syringe. Final concentration will be 1,000 µg/L TPH as Gas.

7.2.4.15 Transfer sample to purging chamber.

7.2.4.16 If an analyte exceeds the calibration range, the sample must be diluted and rerun. Verify that carryover did not occur. If carryover is found to have affected subsequent samples, the system must be decontaminated and the affected samples reanalyzed.

7.2.4.17 Rinse all sample spargers with 3–5 mL rinses of organic free water after sample analysis.

7.2.4.18 The pH of water samples is checked after analysis. The pH should be <2. If the pH isn't <2, it should be noted in the client's report.

7.2.5 EST/Archon Water Sample Analysis

7.2.5.1 For the water GRO/PVOC CVS/LCS, add 40 µL of the EST/Archon 1,000/100 µg/mL CVI / Water Spike Standard to the 40 mL vial. Program the Archon to add 1 µL of the EST/Archon 125 µg/mL Surrogate Standard to the 5 mL aliquot being analyzed. Final concentration for the GRO/PVOC CVS/LCS will be 1,000/100 µg/L GRO/PVOC (based on a 40 mL volume) and final concentration for the surrogate will be 25 µg/L (based on a 5 mL volume).

7.2.5.2 For the water TPH as Gas CVS/LCS, add 100 µL of the EST/Archon 400 µg/mL TPH as Gasoline Calibration Solution / Spike Standard to the 40 mL vial. Program the Archon to add 1 µL of the EST/Archon 125 µg/mL Surrogate Standard to the 5 mL aliquot being analyzed. Final concentration for the TPH as Gasoline CVS will be 1,000 µg/L TPH as Gasoline (based on a 40 mL volume) and final concentration for the surrogate will be 25 µg/L (based on a 5 mL volume).

7.2.5.3 Recoveries for the TPH as Gas CVS/LCS should be ± 15%, the GRO/PVOC CVS/LCS results should be ± 20% or corrective action should be taken. Examples of corrective action may include inspecting the system for leaks, checking for errors in standard preparation or degradation of the standard mix, or evaluating the chromatography system. If major corrective action is required, such as cleaning the detector, lamp, jet or replacing the chromatographic column, a new initial calibration would need to be generated before samples could be analyzed.

7.2.5.4 A method blank is set up per the instructions above without the addition of the CVI. For WI GRO analysis, the method blank must be less than 50 µg/L GRO or the sample batch is re-analyzed if possible. If it is not possible to re-analyze, the data will be flagged where appropriate.

7.2.5.5 Water samples are ready for analysis in the 40 mL vials.

7.2.5.6 Load vials into the Archon autosampler. Program the method to analyze a 5 mL sample volume and add 1 µL of the EST/Archon 125 µg/mL Surrogate Standard to each 5 mL blank, sample, and QC to obtain a 25 µg/L final concentration.

7.2.5.7 For the samples in each analytical batch selected for spiking, add 40 µL of the EST/Archon 1,000/100 µg/mL GRO/PVOC Water Spike Standard, final concentration will be 1,000/100µg/L GRO/PVOC (based on a 5 mL volume). If a batch is analyzed for only TPH as Gas, do a TPH matrix spike by adding 100 µL of the EST/Archon 400 µg/mL TPH as Gasoline Spike Standard to the syringe. Final concentration will be 1,000 µg/L TPH as Gas.

7.2.5.8 The pH of water samples is checked after analysis. The pH should be <2. If the pH isn't <2, it should be noted in the client's report.

7.2.6 Typical Soil Batch

GRO/PVOC
CVS – GRO/PVOC
LCS – GRO/PVOC
Method blank
20 samples
Sample duplicate
MS – PVOC (GRO MS is not quantitated per the method)
LCSD – GRO/PVOC

TPH as Gas/BTEX
CVS/LCS – TPH as Gas
CVS – BTEX
LCS – BTEX
Method blank
20 samples
Sample duplicate
MS – BTEX
LCSD – BTEX
CVS/LCSD – TPH as Gas

TPH as Gas
CVS/LCS –TPH as Gas
Method blank
20 samples
Sample duplicate
MS – TPH as Gas
LCSD – TPH as Gas

7.2.6.1 Station blanks and additional autosampler blanks do not count as samples.

7.2.6.2 Dilutions and reruns performed in the same sequence count as one sample.

7.2.6.3 The CVS/LCS is analyzed at the beginning of the run (if an initial calibration curve was not analyzed).

7.2.7 OI 4650 MPM-16 Soil Sample Analysis

7.2.7.1 Remove the plunger from a 5 mL syringe.

7.2.7.2 Pour reagent water into the syringe barrel.

7.2.7.3 Attach the plunger and compress the sample.

7.2.7.4 Adjust the reagent water volume to 5.0 mL.

7.2.7.5 For the soil GRO/PVOC CVS, add 25 µL of the MPM-16 200/20 µg/mL CVI and 5 µL of the MPM-16 25 µg/mL Surrogate Standard to the syringe. Final concentration for the GRO/PVOC CVS will be 1000/100 µg/L GRO/PVOC and final concentration for the surrogate will be 25 µg/L (based on a 5 mL volume).

7.2.7.6 For the soil TPH as Gasoline CVS, add 100 µL of the MPM-16 50 µg/mL TPH as Gasoline Calibration Solution to the syringe. Final concentration for the TPH as Gasoline CVS will be 1,000 µg/L (based on a 5 mL volume).

7.2.7.7 For the soil GRO/PVOC LCS, add 100 µL of the 50/5 µg/mL GRO/PVOC Soil Spike Standard and 5 µL of the MPM-16 25 µg/mL Surrogate Standard to the syringe. Final concentration for the GRO/PVOC LCS will be 1,000/100 µg/kg GRO/PVOC and final concentration for the surrogate will be 25 µg/L (based on a 5 mL volume).

7.2.7.8 Recoveries for the GRO/PVOC CVS and LCS should be ± 20% or corrective action should be taken. Recoveries for the TPH as Gasoline CVS should be ± 15% or corrective action should be taken. Examples of corrective action may include inspecting the system for leaks, checking for errors in standard preparation or degradation of the standard mix, or evaluating the chromatography system. If major corrective action is required, such as cleaning the detector, lamp, jet or replacing the chromatograph column, a new initial calibration would need to be generated before samples could be analyzed.

7.2.7.9 A method blank is set up containing 100 µL of methanol and 5 µL of the MPM-16 25 µg/mL Surrogate Standard. Final concentration of the surrogate will be 25 µg/L (based on a 5 mL volume). For WI GRO analysis, the method blank must be less than 5 mg/kg GRO or the sample batch is re-analyzed if possible. If it is not possible to re-analyze, the data will be flagged where appropriate.

7.2.7.10 Weigh the tared sample container to determine the actual total weight. If the sample weight is more than 10 g in a 40 mL VOA vial or more than 25 g in a 2 oz jar, add additional methanol at a 1:1 ratio (mL/g).

NOTE: Perform this step immediately before analysis to avoid loss of volatiles caused by poor resealing of the vial.

7.2.7.11 If the sample is received unpreserved, weigh out an aliquot of sample and add an equal volume of methanol to maintain a 1:1 ratio (e.g. 10 g of sample and 10 mL of methanol).

7.2.7.12 Shake the sample for 2 minutes and sonicate for 20 minutes.

7.2.7.13 Allow sediment to settle until a layer of methanol is apparent.

7.2.7.14 Withdraw an appropriate aliquot of the methanol extract (100 µL maximum) and add to organic free water in a luerlock syringe to total 5 mL.

7.2.7.15 For the GRO/PVOC MS sample in each analytical batch selected for spiking, add 100 µL of the 50/5 µg/mL GRO/PVOC Soil Spike Standard and 100 µL of the sample to the syringe. Final concentration will be 1,000/100 µg/L GRO/PVOC (based on a 5 mL volume). If a batch is analyzed for only TPH as Gas, analyze a TPH MS by adding 100 µL of the MPM-16 50 µg/mL TPH as Gasoline Spike Standard to the syringe. Final concentration will be 1,000 µg/L TPH as Gas (based on a 5 mL volume).

7.2.7.16 Add 5 µL of the MPM-16 25 µg/mL Surrogate Standard to each blank, sample, and QC. Final concentration will be 25 µg/L (based on a 5 mL volume).

7.2.7.17 Transfer samples to purging chambers.

7.2.7.18 If an analyte exceeds the calibration range, the sample must be diluted and rerun. Verify that carryover did not occur. If carryover is found to have affected subsequent samples, the system must be decontaminated and the affected samples reanalyzed.

7.2.7.19 Rinse all sample spargers with 3–5 mL rinses of organic free water after sample analysis.

7.2.8 EST/Archon Soil Sample Analysis

7.2.8.1 For the soil GRO/PVOC CVS, add 40 µL of the EST/Archon 1,000/100 µg/mL CVI to the 40 mL vial. Program the Archon to add 1 µL of the EST/Archon 125 µg/mL Surrogate Standard to the 5 mL aliquot being analyzed. Final concentration for the GRO/PVOC CVS will be 1,000/100 µg/L GRO/PVOC (based on a 40 mL volume) and final concentration for the surrogate will be 25 µg/L (based on a 5 mL volume).

7.2.8.2 For the soil TPH as Gasoline CVS, add 100 µL of the EST/Archon 400 µg/mL TPH as Gasoline Calibration Solution to the 40 mL vial. Program the Archon to add 1 µL of the EST/Archon 125 µg/mL Surrogate Standard to the 5 mL aliquot being analyzed. Final concentration for the TPH as Gasoline CVS will be 1,000 µg/L TPH as Gasoline and final concentration for the surrogate will be 25 µg/L (based on a 5 mL volume).

7.2.8.3 For the soil GRO/PVOC LCS, add 800 µL of the 50/5 µg/mL GRO/PVOC Soil Spike Standard to the 40 mL vial. Program the Archon to add 1 µL of the EST/Archon 125 µg/mL Surrogate Standard to the 5 mL aliquot being analyzed. Final concentration for the GRO/PVOC LCS will be 1000/100 µg/L GRO/PVOC (based on a 40 mL volume) and final concentration for the surrogate will be 25 µg/L (based on a 5 mL volume).

7.2.8.4 Recoveries for the GRO/PVOC CVS and LCS should be ± 20% or corrective action should be taken. Recoveries for the TPH as Gasoline CVS should be ± 15% or corrective action should be taken. Examples of corrective action may include inspecting the system for leaks, checking for errors in standard preparation or degradation of the standard mix, or evaluating the chromatography system. If major corrective action is required, such as cleaning the detector, lamp, jet or replacing the chromatograph column, a new initial calibration would need to be generated before samples could be analyzed.

7.2.8.5 A method blank is set up containing 800 µL of methanol and 1 µL of the EST/Archon 125 µg/mL Surrogate Standard. Final concentration of the surrogate will be 25 µg/L (based on a 5 mL volume). For WI GRO analysis, the method blank must be less than 5 mg/kg GRO or the sample batch is re-analyzed if possible. If it is not possible to re-analyze, the data will be flagged where appropriate.

7.2.8.6 Weigh the tared sample container to determine the actual total weight. If the sample weight is more than 10 g in a 40 mL VOA vial or more than 25 g in a 2 oz jar, add additional methanol at a 1:1 ratio (mL/g).

NOTE: Perform this step immediately before analysis to avoid loss of volatiles caused by poor resealing of the vial.

7.2.8.7 If the sample is received unpreserved, weigh out an aliquot of sample and add an equal volume of methanol to maintain a 1:1 ratio (e.g. 10 g of sample and 10 mL of methanol).

7.2.8.8 Shake the sample for 2 minutes and sonicate for 20 minutes.

7.2.8.9 Allow sediment to settle until a layer of methanol is apparent.

7.2.8.10 Withdraw an appropriate aliquot of the methanol extract (800 µL maximum) and add to 40 mL organic free water in a VOA vial.

7.2.8.11 For the GRO/PVOC MS sample in each analytical batch selected for spiking, add 800 µL of the 50/5 µg/mL GRO/PVOC Soil Spike Standard and 800 µL of the sample to 40 mL organic free water in a VOA vial. Final concentration will be 1,000/100 µg/L GRO/PVOC (based on a 40 mL volume). If a batch is analyzed for only TPH as Gas, analyze a TPH MS by adding 100 µL of the EST/Archon 400 µg/mL TPH as Gasoline Spike Standard to 40 mL organic free water in a VOA vial. Final concentration will be 1,000 µg/L TPH as Gas (based on a 40 mL volume).

7.2.8.12 Load vials into the Archon autosampler. Program the method to analyze a 5 mL sample volume and add 1 µL of the EST/Archon 125 µg/mL Surrogate Standard to each 5 mL blank, sample, and QC to obtain a 25 µg/L final concentration.

7.3 Calculation

7.3.1 Retention Time Window and Quantitation

7.3.1.1 GRO equals the sum of all peaks eluting between MTBE and naphthalene. Quantitation is based on a direct comparison of the area within this range to the total area of the 10 components in the GRO standard.

7.3.1.2 Determine the retention time window for the first and last compounds on each GC column and whenever a new column is installed. The retention time window is approximately 0.1 minute before MTBE and ends at 0.1 minute after the retention time of naphthalene. These data are entered into the ICAL. Check the window daily. Adjust the retention time window, if necessary.

7.3.1.3 Analysis of benzene, methyl-tert-butyl ether, toluene, ethyl benzene, total xylenes, naphthalene, and the trimethylbenzenes may also be determined by this method if the PID and FID are connected in series. Quantitation is based on the individual response from the photoionization detector using an external standard method.

7.3.1.4 GRO and TPH as Gas are determined by peak summation on the flame ionization detector using an external standard method.

7.3.2 Calculate the concentration of analytes in the sample using one of the following equations:

$$Water\ Concentration\ (\mu g / L) = (C)(F)$$

C = On-column concentration, µg/L
F = Dilution factor

$$Soil\ Concentration\ (mg / kg) = \frac{(C)(V_m)(V_t)(F)}{(V_i)(W)(1{,}000)(D)}$$

C = On-column concentration, µg/L
V_m = Volume of methanol, mL
V_t = Total volume purged, mL
F = Dilution factor
V_i = Volume of sample extract added for purging, mL
W = Weight of sample (g)
D = % dry weight of sample/100, or 1 for wet weight basis

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, when there is a change in the test method that may affect how the test is performed or when there is a major change in instrumentation. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. For GRO analysis, the method blank must be less than 50 µg/L for waters and less than 5 mg/kg for soils or the sample batch is re-analyzed if possible. If it is not possible to re-analyze, the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Accuracy control limits are set at 80.0-120% except for the TPH as Gasoline CVS which is set at 85.0-115%. Surrogate limits are set at 80.0-150%. No maximum surrogate recovery is specified in the method due to coelution occurring with high sample amounts. Surrogate recoveries greater than 120% in samples without high amounts may be reanalyzed at the analyst's discretion.

9.3.2 Precision control limits are set at $< 20\%$ RPD.

9.3.3 QC calculations are found in the QA Manual

9.3.4 LCS, MS, duplicates and surrogates are reviewed.

9.3.5 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is reanalyzed if possible. If the batch cannot be reanalyzed, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.6 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS is flagged and/or a case narrative is written.

9.3.7 If the duplicate data are outside the limits, the data for that specific duplicate is flagged and/or a case narrative is written.

9.3.8 If a sample surrogate is outside the limits, the sample is reanalyzed if possible. If the sample cannot be reanalyzed, the data is flagged next to the actual result in the report.

10. REPORTING

10.1 Soil samples results are reported in mg/kg on a dry weight basis.

10.2 For GRO analysis, if a soil sample is received in a 40 mL VOA vial with an initial weight greater than 20 grams or in a 2 oz jar with an initial weight greater than 35 grams, the WI(95)GRO method requires rejection of the sample unless the client requests the analysis. The sample result cannot be considered GRO and will be reported as C6-C10.

10.3 For GRO analysis, if a soil sample is received with an initial weight less than 8 grams in a 40 mL VOA vial or less than 20 grams in a 2 oz jar, the result will be flagged.

10.4 Water sample results are reported in µg/L.

10.5 The reported result is rounded to two significant figures.

10.6 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

12. REFERENCES

12.1 Wisconsin DNR Modified GRO Method PUBL-SW-140

12.2 EPA Methods 8000, 8015B and 8021B

Appendix A

Initial Demonstration of Capability (IDC)
GRO/PVOC

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare five replicate GRO/PVOC spikes in water at a concentration of 100 µg/L and/or five replicate GRO/PVOC spikes in soil at a concentration of 10 mg/kg.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC DRO GRO', the individual results are entered. The individual recoveries and the %RSD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: Soil = 75.0-120%, Water = 80.0-120%
   Precision: $\leq$ 20% RSD

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee's personnel folder. An acceptable IDC for GRO/PVOC also qualifies an analyst for TPH as Gasoline.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
GRO/PVOC

Parameter	Water MDL (µg/L)	Water RL (µg/L)	Soil MDL (mg/kg)	Soil RL (mg/kg)
GRO	7.4	100	0.37	5.0
MTBE	0.22	5.0	0.0060	0.025
Benzene	0.16	1.0	0.0060	0.025
Toluene	0.10	1.0	0.0047	0.025
Ethyl benzene	0.15	1.0	0.0030	0.025
Total xylenes	0.28	3.0	0.0050	0.075
1,3,5-Trimethylbenzene	0.12	1.0	0.0061	0.025
1,2,4-Trimethylbenzene	0.22	1.0	0.0034	0.025
Naphthalene	0.23	5.0	0.042	0.50

Method Detection Limits and Reporting Limits
TPH as Gasoline

Parameter	Water MDL (µg/L)	Water RL (µg/L)	Soil MDL (mg/kg)	Soil RL (mg/kg)
TPH as Gasoline	22	150	0.41	10

DOCUMENT REVIEW

DOCUMENT:	SOP LABENV-010.5
REVIEWER:	Yen Pham
DATE:	03/12/09

SECTION	**CHANGE**	**RATIONALE**
Appendix B	MDLs updated	Annual update

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: ANALYSIS OF ALKALINITY AS $CaCO_3$ IN WATER

SOP NO.: LABENV-012.6

Original Information		
Prepared by:	Rose Breiland	Date: 08/18/92
Technical Review:	Corine Goodrich	Date: 08/18/92
QA/QC Coordinator:		Date:
Authorized by:	Cheryl Sykora	Date: 08/18/92

Revision Information		
Supersedes:	LABENV-012.5	Date: 08/22/07
Revised by:	Jaime Zwers	Date: 04/02/08
Signature:	______________________	Date: __________
Technical Review:	Cynthia Schultz	Date: 04/03/08
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 04/04/08
Signature:	______________________	Date: __________

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LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: ANALYSIS OF ALKALINITY AS $CaCO_3$ IN WATER

SOP NO.: LABENV-012.6

Original Information		
Prepared by:	Rose Breiland	Date: 08/18/92
Technical Review:	Corine Goodrich	Date: 08/18/92
QA/QC Coordinator:		Date:
Authorized by:	Cheryl Sykora	Date: 08/18/92

Revision Information		
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Revised by:	Jaime Zwers	Date:
Signature:		Date:
Technical Review:	Cynthia Schultz	Date:
Signature:		Date:
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 4/04/08

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FORM GEN-021 (05/07)

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: ANALYSIS OF ALKALINITY AS $CaCO_3$ IN WATER
SOP NO.: LABENV-012.6

Original Information		
Prepared by:	Rose Breiland	Date: 08/18/92
Technical Review:	Corine Goodrich	Date: 08/18/92
QA/QC Coordinator:		Date:
Authorized by:	Cheryl Sykora	Date: 08/18/92

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Revised by:	Jaime Zwers	Date:
Signature:	[signature]	Date: 4/2/08
Technical Review:	Cynthia Schultz	Date:
Signature:	[signature]	Date: 4/3/08
Authorized by:	Cheryl Sykora	Date:
Signature:		Date:

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FORM GEN-021 (05/07)

SOP TITLE: ANALYSIS OF ALKALINITY AS $CaCO_3$ IN WATER

1. PURPOSE

1.1 This document defines the procedure to be followed when determining alkalinity in waters and wastewaters using an end-point pH of 4.5 su. The SOP is applicable to samples typically analyzed by Standard Methods (SM) 2320 B, Online Version, 1997.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the standard operating procedure.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This method is applicable to aqueous samples only.

3.2 This method is not applicable to samples that require results below 20 mg/L. Alkalinity as $CaCO_3$ can be reported less than 20 mg/L only if it has been determined by the low-level method.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 Gloves and safety glasses should be worn.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Samples should be collected in an unpreserved glass/plastic container and stored at 4 ± 2 °C.

5.4 The recommended holding time for samples is 14 days until analysis.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 Standard sulfuric acid solution, 0.02 N, commercially prepared and certified

6.2 Bromocresol green-methyl red indicator solution, commercially prepared

6.3 pH meter, Orion EA 940 or equivalent

6.4 50 mL graduated cylinder

6.5 Buret, 50 mL with 0.1 mL graduations

6.6 Assorted laboratory glassware

6.7 Deionized (DI) water (>16 MΩ)

6.8 Check Standard (Na_2CO_3) – dissolve 106-159 mg of Na_2CO_3 to 500 mL of deionized water to produce a 200-300 ppm solution (1 mg/L Na_2CO_3 = 0.9434 mg/L $CaCO_3$) – freshly prepare once a year, sooner if results indicate a problem

6.9 Reporting Limit Verification (RLV) Standard (Na_2CO_3) – dissolve 10.6 mg of Na_2CO_3 to 500 mL of deionized water to produce a 20 ppm solution (1 mg/L Na_2CO_3 = 0.9434 mg/L $CaCO_3$) – freshly prepare once a year, sooner if results indicate a problem

7. PROCEDURE

7.1 Calibration

7.1.1 The pH meter should be calibrated at pH 4, 7, and 10 prior to each use (see SOP ‘Analysis of pH by Electrometric Method’).

7.2 Analysis

7.2.1 Record the project and sample numbers in the Alkalinity Logbook.

7.2.2 Using a 50 mL graduated cylinder, add 50 mL of DI water (method blank) to a labeled 250 mL Erlenmeyer flask. The method blank will be carried through all steps and used as the end-point color reference (slight pink to red).

7.2.3 Using a 50 mL graduated cylinder, add 50 mL of the check standard to a labeled 250 mL Erlenmeyer flask. Recovery of the check standard should be ± 10% or corrective action is taken.

7.2.4 Corrective action may include but is not limited to reanalyzing the check standard, preparing and analyzing a new check standard, and/or using new reagents.

7.2.5 Using a 50 mL graduated cylinder, add 50 mL of the RLV Standard to a labeled 250 mL Erlenmeyer flask.

7.2.5.1 Reporting limit verification (RLV) is checked monthly at a minimum by analyzing a standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.2.6 Using a 50 mL graduated cylinder, add 50 mL of each sample to a labeled 250 mL Erlenmeyer flask.

7.2.7 One duplicate sample is to be analyzed per batch of 10 or fewer samples.

7.2.8 Record the sample volumes in the Alkalinity Logbook.

7.2.9 Determine the pH of each sample with the pH meter and record in the Alkalinity Logbook.

7.2.10 Add 4-5 drops of bromocresol green-methyl red indicator to each Erlenmeyer flask.

7.2.11 Rinse buret with 0.02N sulfuric acid, fill past the 50 mL mark and deliver acid into a waste container to the zero mark.

7.2.12 While swirling the flask, titrate each sample.

7.2.13 As end-point is approached make smaller additions of acid, and make sure pH equilibrium is attained before adding more titrant.

7.2.14 Record volume of titrant used.

7.2.15 If turbidity or excess suspended solids in the sample interfere with indicator color change, transfer sample into a 200 mL beaker and determine alkalinity using a pH meter to an end-point of 4.5 su.

7.3 Calculation

$$\textit{Alkalinity, mg } CaCO_3/L = \frac{(A)(N)(50{,}000)}{\textit{mL sample}}$$

where:

A = amount of standard acid titrated, mL
N = normality of standard acid

8. WASTE DISPOSAL

8.1 Samples and analysis materials are disposed of in accordance with current company waste disposal procedures.

8.2 Highly contaminated samples are returned to the client for disposal.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, on an annual basis. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed. The RL for alkalinity is set at 20 mg/L based on the reference method.

9.2 Method Blank

9.2.1 The method blank must be less than the reporting limit or the batch is reanalyzed if possible. If it is not possible to reanalyze the batch, the data will be flagged. Do not subtract the blank result from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 The precision limit between the sample/sample duplicate must be $\leq$ 20% RPD or the batch is reanalyzed if possible. If it is not possible to reanalyze the batch, the data will be flagged.

9.3.2 QC calculations are found in the QA Manual

10. REPORTING

10.1 Water sample results are reported in mg/L.

10.2 The reported result is rounded to two significant figures.

10.3 The results are placed in the client file and a final report is sent to the client.

10.4 The reporting limit for this analysis is 20 mg/L based on methodology.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

12. REFERENCES

12.1 Standard Methods for the Examination of Water and Wastewater, Method 2320 B, Online Version, 1997

12.2 Orion EA 940 Expandable Ion Analyzer Instruction Manual

Appendix A

Initial Demonstration of Capability (IDC)
Alkalinity as $CaCO_3$ in Water

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four replicate standards between 20-1000 mg/L in lab-grade water and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: 90.0-110%
   Precision: $\leq$20.0% RPD

7. The reagent blank must be less than the reporting limit (RL).

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
Alkalinity as $CaCO_3$ in Water

Parameter	Water MDL (mg/L)	Water RL (mg/L)
Total Alkalinity	5.7	20

DOCUMENT REVIEW

DOCUMENT:	LABENV-012.6
REVIEWER:	Jaime Zwers
DATE:	03/12/08

SECTION	CHANGES
Appendix B	Updated MDL

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF DIESEL RANGE ORGANICS (DRO)

SOP NO.: LABENV-007.9

Original Information		
Prepared by:	Chris Bremer	Date: 07/28/92
Technical Review:	Corrine Goodrich	Date: 08/05/92
QA/QC Coordinator:		Date:
Authorized by:	Cheryl Sykora	Date: 07/28/92

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Revised by:	Bouakhine Vongphachan	Date: 03/16/09
Signature:	______________________	Date: __________
Technical Review:	Triet Le	Date: 03/17/09
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 03/17/09
Signature:	______________________	Date: __________

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LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF DIESEL RANGE ORGANICS (DRO)
SOP NO.: LABENV-007.9

Original Information		
Prepared by:	Chris Bremer	Date: 07/28/92
Technical Review:	Corrine Goodrich	Date: 08/05/92
QA/QC Coordinator:		Date:
Authorized by:	Cheryl Sykora	Date: 07/28/92

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Signature:	[signature]	Date: 3/16/09
Technical Review:	Triet Le	Date:
Signature:	[signature]	Date: 3/17/09
Authorized by:	Cheryl Sykora	Date:
Signature:	[signature]	Date: 3/17/09

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FORM GEN-021 (05/07)

SOP TITLE: DETERMINATION OF DIESEL RANGE ORGANICS (DRO)

1. PURPOSE

1.1 This document defines the preparation and analysis to be followed for Diesel Range Organics (DRO) in soil and water by gas chromatography (GC) using a Flame Ionization Detector (FID). The SOP is applicable to samples typically analyzed by Wisconsin DNR Modified DRO Method, PUBL-SW-141.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the standard operating procedure.

2.3 Analysts trained in GC/FID techniques by Legend Technical Services, Inc. (LEGEND) shall perform this analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 Any peak found in the DRO window should be calculated as DRO. If there are significant peaks outside of this window, the data should be flagged. An “M” flag signifies that lower boiling point compounds are present in the sample and an “L1” flag signifies that there are higher boiling point compounds present in the sample.

4. HEALTH AND SAFETY

4.1 Review all Material Safety Data Sheets (MSDS) for chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 A lab coat and safety glasses should be worn.

4.4 When working with organic compounds, solvent resistant gloves should be worn.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample’s integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample’s integrity.

5.3 Water samples should be collected in 1L amber bottles with Teflon lined caps preserved with 5 mL of 50% HCl and stored at 4 ± 2 °C.

5.4 The recommended holding time for water samples is 7 days until extraction and analysis within 47 days of collection.

5.5 Soil samples should be collected in pre-weighed 4 oz glass jars with Teflon lined caps and stored at 4 ± 2 °C. Soil samples should be received at the laboratory within 10 days of collection.

5.6 The recommended holding time for soil samples is 10 days until extraction solvent is added and analysis within 47 days of collection.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 HP 5890 Series II Gas Chromatograph equipped with a flame ionization detector (FID) and a data processing system

6.2 Restek Rtx®-5MS: 30 m x 0.53 mm x 1.5 µm film capillary column, or equivalent

6.3 Equatherm Orbit Shaker or equivalent

6.4 Ultrasonic bath

6.5 Nitrogen evaporator – N-EVAP or equivalent

6.6 500 mL K-D flask

6.7 Snyder columns

6.8 Turbo Vap II and associated parts and glassware

6.9 2 liter separatory funnel

6.10 Analytical balance, capable of reading to 0.01 g

6.11 Microliter syringes

6.12 Volumetric flasks, 100 mL, 50 mL, 25 mL

6.13 Graduated cylinder, 1000 mL

6.14 Disposable pipets

6.15 Filter paper – Whatman 41 or equivalent

6.16 10 mL K-D concentrators

6.17 Steam bath

6.18 Glass funnels

6.19 Glass wool

6.20 PTFE solvent rinsed boiling beads, or equivalent

6.21 4 mL saver vials with Teflon liner

6.22 2 mL autosampler vials

6.23 pH paper (0-14 Std. Units)

6.24 Organic free water

6.25 Ottawa Sand (20-30 mesh) or equivalent – muffle at 400 °C for four hours before using

6.26 Acetone – pesticide grade or equivalent

6.27 Hexane – pesticide grade or equivalent

6.28 Methanol – pesticide grade or equivalent

6.29 Iso-octane – pesticide grade or equivalent

6.30 Methylene chloride – pesticide grade, or equivalent

6.31 Anhydrous Sodium Sulfate (Na_2SO_4) – muffle at 400 ºC for four hours before using

6.32 DRO Stock A – purchase standard containing the specific diesel components (Decane, Dodecane, Tetradecane, Hexadecane, Octadecane, Eicosane, Decosane, Tetracosane, Hexacosane, and Octacosane), 20,000 µg/mL, store in freezer and protect from light, Restek #31064 or equivalent

6.33 DRO Stock B – purchase standard containing the specific diesel components (Decane, Dodecane, Tetradecane, Hexadecane, Octadecane, Eicosane, Decosane, Tetracosane, Hexacosane, and Octacosane), 20,000 µg/mL, store in freezer and protect from light, Absolute #90322 or equivalent – Restek Stock may be used but it must be a different lot number than stock used in the calibration curve

6.34 Surrogate Stock – Triacontane (C_{30}) 98%, 1 gram (ACROS #278050010, or equivalent)

6.35 Spike Standard – dilute 2.0 mL of the 20,000 µg/mL DRO Stock B to 25 mL with 1:1 methanol:methylene chloride to produce a 1,600 µg/mL solution, store in inorganic freezer.

6.36 Working Surrogate Standard – add 40.0 mg of Surrogate Stock (Triacontane) to 20 mL Iso-octane in a 100 mL volumetric flask, sonicate for 30 minutes or until the triacontane is dissolved, and dilute to 100 mL final volume with 1:1 methanol:methylene chloride to produce a 400 µg/mL solution. Store in inorganic freezer.

6.37 Working Calibration Surrogate Standard – add 25.0 mg of Surrogate Stock (Triacontane) to 10 mL Iso-octane in a 50 mL volumetric flask and sonicate for 30 minutes or until the triacontane is dissolved, and dilute to 50 mL final volume with 1:1 methanol:methylene chloride to produce a 500 µg/mL surrogate solution. Store in inorganic freezer.

6.38 Calibration Intermediate Standard – combine 400 µL of the 20,000 µg/mL DRO Stock A and 1.6 mL of the Working Calibration Surrogate Standard into a keeper vial to produce a solution of 4000 µg/mL DRO and 400 µg/mL surrogate

6.39 Calibration Verification Standard (CVS) – dilute 500 µL of the 20,000 µg/mL DRO Stock B and 2 mL of the 500 µg/mL Working Calibration Surrogate Standard to 10 mL with methylene chloride to produce a solution at 1,000 µg/mL DRO and 100 µg/mL surrogate and store in freezer

7. PROCEDURE

7.1 Preparation of Water Samples

7.1.1 Pre-rinse all extraction glassware with acetone, hexane, and methylene chloride.

7.1.2 Mark the water level on the outside of the bottle for later determination of volume.

7.1.3 Measure the pH of the sample and note on the extraction sheet. The pH should be less than 2. Transfer sample to a pre-rinsed 2 L Separatory Funnel. (Note: If an evident layer of sediment is present, decant the sample and record on the extraction sheet.)

7.1.4 Use 1000 mL organic free water for each blank, Laboratory Control Sample (LCS), and Laboratory Control Sample Duplicate (LCSD).

7.1.5 Add 1.0 mL of the 400 µg/mL Working Surrogate Standard to each funnel. Final concentration will be 400 µg/L assuming a 2 mL final volume and 1,000 mL sample volume.

7.1.6 Add 1.0 mL of the 1,600 µg/mL Spike Standard to the LCS and LCSD. Final concentration will be 1,600 µg/L assuming a 2 mL final volume and 1,000 mL sample volume.

7.1.7 Add 60 mL of methylene chloride to the sample bottle and rinse. Transfer to the separatory funnel with the sample. (NOTE: If the sample was decanted, add the 60 mL of methylene chloride directly to the separatory funnel.)

7.1.8 Cap and shake vigorously for 10 seconds and then vent. Cap and shake for 2 minutes. Allow the methylene chloride to separate from the sample.

7.1.9 If an emulsion interface between the layers is more than one-third the size of the solvent layer, the analyst should employ mechanical techniques to complete the phase separation. Refer to the protocol found in Work Instruction (WI) 'Handling Emulsions'.

7.1.10 Transfer the solvent layer to a pre-rinsed glass funnel containing a glass wool plug and about 2-3 inches of anhydrous muffled Na_2SO_4 Allow to drain into a 500 mL K-D flask equipped with a 10 mL K-D concentrator for Nitrogen Blowdown. Rinse after each addition of methylene chloride.

7.1.11 Repeat steps above with 60 mL of fresh solvent.

7.1.12 Fill sample bottle with tap water to the mark made previously. Transfer to a graduated cylinder and record volume on extraction sheet.

7.1.13 K-D Technique / Nitrogen Blowdown

7.1.13.1 Add one solvent rinsed boiling bead to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-85 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot vapor. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 4 mL, remove the K-D apparatus from the water bath and allow it to drain and cool.

7.1.13.2 Put the K-D concentrator in a warm bath (about 35 °C) and evaporate the solvent volume to less than 2 mL using a gentle stream of clean, dry nitrogen. During evaporation, the tube solvent level must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Do not allow the extract to go dry. Using a disposable pipet, adjust the final volume to 2.0 mL with methylene chloride and mix the extract completely.

7.1.13.3 Transfer approximately 1 mL to a 2 mL autosampler vial and put the rest in an autosampler vial. Store in freezer until analysis.

7.1.14 Silica Gel Cleanup

7.1.14.1 If a sample requires silica gel cleanup refer to the protocol found in Work Instruction (WI) 'Dro Silica Gel Cleanup Procedure'.

7.2 Preparation of Soil Samples

7.2.1 Check sample weigh sheet prior to adding solvent to make certain the weight of the sample is 25-70 grams in a 4 oz jar or 25-35 grams in a 2 oz jar.

NOTE: If sample is not received in a preweighed 4 oz or 2 oz jar, contact the client manager or laboratory supervisor for further information.

7.2.2 Pre-rinse all extraction glassware with acetone, hexane, and methylene chloride.

7.2.3 Add approximately 25 g of anhydrous muffled Na_2SO_4 to the sample and mix with a steel spatula. Additional Na_2SO_4 may be required to dry the sample if the sample is visibly wet.

7.2.4 Add 25 mL of methylene chloride, or a 1:1 ratio of methylene chloride to grams of sample, whichever is greater, to the soil jar. This should be performed within 10 days of sample collection.

7.2.5 Add 1.0 mL of the 400 µg/mL Working Surrogate Standard to each jar. Final concentration will be 16 mg/kg assuming a 4 mL final volume and 25 g sample amount.

7.2.6 Add 1.0 mL of the 1,600 µg/mL Spike Standard to the LCS and LCSD. Final concentration will be 64 mg/kg assuming a 4 mL final volume and 25 g sample amount.

7.2.7 Shake for 2 minutes using the Equatherm Orbit Shaker.

7.2.8 Sonicate for approximately 20 minutes.

7.2.9 Allow sediment to settle until a solvent layer is apparent.

7.2.10 Remove solvent with a glass disposable pipet and transfer into a glass funnel containing filter paper and sitting atop a 500 mL Kuderna-Danish concentrator or a 200 mL Turbo Vap II concentration vial. (Note: When dealing with dark extracts use a glass funnel containing anhydrous muffled Na_2SO_4.)

7.2.11 Repeat above steps with the same amount of fresh solvent. Remove the second aliquot of solvent with a glass disposable pipet and add the solvent to the funnel.

7.2.12 Add the soil to the funnel and rinse the sample jar three times with methylene chloride, adding the rinsate to the funnel each time.

7.2.13 If the second aliquot of methylene chloride used to extract the sample was still dark in color, continue to rinse the sample until the methylene chloride is clear. Do not use more than 200 mL methylene chloride. Make certain to note additional solvent on extraction sheet.

7.2.14 K-D Technique / Nitrogen Blowdown

7.2.14.1 Add one solvent rinsed boiling bead to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-85 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot vapor. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

7.2.14.2 When the apparent volume of liquid reaches 4 mL, remove the K-D apparatus from the water bath and allow it to drain and cool.

7.2.14.3 Put the K-D concentrator in a warm bath (about 35 °C) and evaporate the solvent volume to less than 4 mL using a gentle stream of clean, dry nitrogen. During evaporation, the tube solvent level must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Do not allow the extract to go dry. Using a disposable pipet, adjust the final volume to 4.0 mL with methylene chloride and mix the extract completely.

7.2.14.4 Transfer approximately 1 mL to a 2 mL autosampler vial and put the rest in a 4 mL saver vial. Store in freezer until analysis.

7.2.15 Turbo Vap II

7.2.15.1 Place the Turbo Vap collection tube in the Turbo Vap.

7.2.15.2 Set the water bath temperature to 40 °C and the pressure to 8-12 psi.

7.2.15.3 Set the Turbo Vap to monitor by ‘sensor’ to achieve a final volume of approximately 3 mL.

7.2.15.4 Using a disposable pipet, adjust the final volume to 4.0 mL with methylene chloride and mix the extract completely. Transfer approximately 1 mL to a 2 mL autosampler vial and the remaining extract to a 4 mL saver vial. Store in freezer until analysis.

7.2.16 Silica Gel Cleanup

7.2.16.1 If a sample requires silica gel cleanup refer to the protocol found in Work Instruction (WI) 'Dro Silica Gel Cleanup Procedure'.

7.3 Calibration

7.3.1 Prepare working standards at a minimum of 5 concentration levels, ranging from 50-3000 µg/mL, by diluting the 4000 µg/mL Calibration Intermediate Standard with methylene chloride to a final volume of 1.0 mL. A typical calibration curve would be:

Inter. Std. (µL)	Methylene Chloride (µL)	DRO Conc. (µg/mL)	Surrogate Conc. (µg/mL)
12.5	987.5	50	5
25	975	100	10
50	950	200	20
125	875	500	50
250	750	1000	100
500	500	2000	200
750	250	3000	300

7.3.2 Prepare a calibration curve of concentration vs. response. The correlation coefficient (r) should be 0.990 or better.

7.3.3 Calibration curve calculations are found in the QA Manual.

7.3.4 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.3.5 The concentrations define the working range of the detector and expected range of the sample results.

7.4 Analysis

7.4.1 GC Conditions (FID4, FID5, FID6)

7.4.1.1 Column: RTx® - 5MS 30m x 0.53 mm ID x 1.5 µm film, or equivalent

7.4.1.2 Injector Temp: 280 °C

7.4.1.3 Detector Temp: 310 °C

7.4.1.4 Temp. Program: hold at 75 °C for 0.5 min, increase 15 °C/min to 300 °C and hold 10 min

7.4.1.5 GC Range: 3

7.4.1.6 Attenuation: 0

7.4.1.7 Injection Volume: 1.0 µL

7.4.1.8 Constant Flow: On at 8.0 mL/min (FID5, not applicable to FID4 and FID6)

7.4.2 The initial calibration curve (ICAL) should be verified each day and every 20th injection, by injecting a mid-level standard (CVS) prepared from a second source. Recoveries should be ± 20% or corrective action should be taken. Corrective action may include reinjection, maintenance, flagging the data, and/or preparing a new initial calibration curve.

7.4.3 LCS and LCSD runs must bracket samples during the GC run. Reruns and/or dilutions of samples within an extraction batch do not need to be bracketed by the LCS and LCSD.

7.4.4 If the response for the peak area of the sample exceeds the highest calibration standard, dilute the extract with methylene chloride and re-analyze.

7.4.5 Retention Time Window and Quantitation

7.4.5.1 The retention time window is defined as beginning approximately 0.1 minutes before the onset of the n-decane peak and ending 0.1 minutes after the conclusion of the n-octacosane peak in the calibration run.

7.4.5.2 Check retention time window at the beginning of every day to insure a retention time shift has not occurred or corrective action must be taken. Corrective action may include updating the retention time window using the CVS, instrument maintenance and/or preparing a new initial calibration curve.

7.4.5.3 Quantitation of DRO is determined from a summation of the total response within the retention time window established for n-decane and n-octacosane, using the calibration curve. No area may be subtracted from the DRO retention time window in calculating DRO results.

7.4.6 Integration must be “baseline to baseline” as opposed to a “valley to valley”. Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of chromatographic graph that includes all responses within the retention time window. The correct baseline placement would be a horizontal line drawn through the lowest point in the chromatogram (before the end of the window). The lowest point may be within the window, outside the window (on the early end of the window), or before the solvent front. Baseline to baseline integration does not include the solvent peak.

7.5 Calculation

7.5.1 Compute the concentration of the analyte in the sample using one of the following equations:

$$Water\ Concentration\ (\mu g/L) = \frac{(C_{ex})(V_{ex})(F)}{V_o}$$

$$Soil\ Concentration\ (mg/kg) = \frac{(C_{ex})(V_{ex})(F)}{(W_s)(D)}$$

C_{ex} = extract concentration, µg/mL
V_{ex} = extract volume, mL
F = dilution factor (diluted volume/extract volume)
V_o = volume of sample extracted, L
W_s = sample weight, g
D = % dry weight of sample/100, or 1 for wet weight basis

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, when there is a change in the test method that may affect how the test is performed or when there is a major change in instrumentation. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. For DRO analysis, the method blank must be less than 50 µg/L for waters and less than 5 mg/kg for soils. If this is not true, the sample batch is re-analyzed if possible. If it is not possible to re-analyze, the information is placed in the daily and project files and the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Method accuracy and precision limits are used for compliance (see Appendix C) except surrogate limits which are generated semi-annually, using 20 Percent Recovery points, as follows:

9.3.1.1 Upper and Lower Control Limit = Mean ± 3s

9.3.1.2 Upper and Lower Warning Limit = Mean ± 2s

9.3.1.3 s = Standard deviation

9.3.2 QC calculations are found in the QA Manual

9.3.3 LCS, duplicate results and surrogates are reviewed.

9.3.4 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is re-extracted and/or reanalyzed if possible. If the batch cannot be re-extracted and/or reanalyzed, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.5 If the duplicate data are outside the limits (the LCS has already been reviewed and is acceptable), the data for that specific duplicate is flagged and/or a case narrative is written.

9.3.6 If a sample surrogate is outside the limits, the sample is re-extracted and/or reanalyzed if possible. If the sample cannot be re-extracted and/or reanalyzed, the data is flagged next to the actual result in the report.

10. REPORTING

10.1 Soil sample results are reported in mg/kg on a dry weight basis.

10.2 If a soil sample is received in a 4 oz jar with an initial weight greater than 70 grams or in a 2 oz jar with an initial weight greater than 35 grams, the WI(95)DRO method requires rejection of the sample unless the client requests the analysis. The sample result cannot be considered DRO and will be reported as C10-C28.

10.3 Water sample results are reported in µg/L.

10.4 The reported result is rounded to two significant figures.

10.5 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

11.3 Appendix C – Method Limits for WI DRO

12. REFERENCES

12.1 Wisconsin Department of Natural Resources Leaking Underground Storage Tank (LUST) Analytical Guidance document, April 1992 PUBL-SW-130 92 REV

12.2 Wisconsin DNR Modified DRO - Method for Determining Diesel Range Organics, PUBL-SW-141

12.3 Vendor operating manuals

Appendix A

Initial Demonstration of Capability (IDC)
Wisconsin DNR Modified DRO

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare five DRO spikes in water at a concentration of 100 µg/L and/or five DRO spikes in soil at a concentration of 10 mg/kg and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form ‘IDC DRO GRO’ the individual results are entered. The individual recoveries and the % RSD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: Soil = 70.0-120%, Water = 75.0-115%
   Precision: $\leq$ 20% RSD

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee’s personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
WI DRO

Parameter	Water MDL (µg/L)	Water RL (µg/L)	Soil MDL (mg/kg)	Soil RL (mg/kg)
DRO	26	100	1.9	8.0

Appendix C

Method Spike Recovery Limits
WI DRO

Parameter	Accuracy Method Limits (%)	Precision Method Limits (%RPD)
Water	75 - 115	20
Soil	70 - 120	20

DOCUMENT REVIEW

DOCUMENT:	LABENV-007.9
REVIEWER:	Bouakhine Vongphachan
DATE:	01/27/09

SECTION	CHANGE	RATIONALE
6.3	Added ‘Equatherm Orbit Shaker or equivalent’	Soils samples require shaking
7.2.7	Inserted subsection	Soils samples require shaking
Appendix B	Updated MDLs	Annual update

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: ANALYSIS OF SAMPLES BY ICP-MS

SOP NO.: LABENV-066.1

Original Information		
Prepared by:	Cynthia Schultz	Date: 05/11/07
Technical Review:	Jaime Zwers	Date: 05/11/07
QA/QC Coordinator:	Lisa Bloomgren	Date: 05/11/07
Authorized by:	Cheryl Sykora	Date: 05/14/07

Revision Information		
Supersedes:	LABENV-066	Date: 05/14/07
Revised by:	Jaime Zwers	Date: 08/28/08
Signature:	________________	Date: ________
Technical Review:	Tammika Shedd	Date: 08/28/08
Signature:	________________	Date: ________
Authorized by:	Cheryl Sykora	Date: 09/02/08
Signature:	________________	Date: ________

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Authorized by:	Cheryl Sykora	Date: 05/14/07

Revision Information		
Supersedes:	LABENV-066	Date: 05/14/07
Revised by:	Jaime Zwers	Date:
Signature:	Jaime Zwers	Date: 8/28/08
Technical Review:	Tammika Shedd	Date:
Signature:	[signature]	Date: 08/28/08
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 9/2/08

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FORM GEN-021 (05/07)

SOP TITLE: ANALYSIS OF SAMPLES BY ICP-MS

1. PURPOSE

1.1 This document defines the procedure to be followed for analyzing samples by inductively coupled plasma mass spectrometry (ICP-MS). The SOP is applicable to wastewater, non-potable water, solid and chemical materials, samples typically analyzed by methods EPA 200.8 and EPA 6020.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the standard operating procedure.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This SOP is applicable to aqueous samples or digestates of various matrices.

3.2 Sample digests containing more than 0.2% solids may cause interference by blocking the nebulizer flow or plugging the cones. The digests should be diluted prior to analysis.

3.3 Samples with high in-solution element concentrations must be diluted prior to analysis to avoid damaging the instrument's detector.

3.4 The instrument is optimized to correct for known interferences. Non-routine analyses may require additional method development and interference checks.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 When working with chemicals, wear safety glasses and appropriate gloves.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Water samples should be collected in polyethylene or glass containers and preserved with 1:1 nitric acid to a pH < 2. Samples to be filtered in the laboratory should be collected in an unpreserved bottle.

5.4 If a water sample is received with pH > 2 and does not require filtration by the laboratory, it is preserved in the laboratory and allowed to sit for a minimum of 24 hours at which time the pH is re-tested. If pH < 2, proceed. If not, repeat until pH is < 2, if possible. Highly alkaline samples may need to be digested at a reduced volume with excess acid, rather than diluting the original sample in an attempt to lower the pH.

5.5 Soil samples should be collected in polyethylene or glass containers and stored at 4 ± 2 ºC.

5.6 The recommended holding time for water and soil samples is six months.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 Varian ICP-MS, or equivalent

6.2 Varian Model SPS-3™ Autosampler, or equivalent

6.3 15 mL disposable polyethylene tubes

6.4 Assorted polytetrafluoroethylene (PTFE) lab-ware

6.5 Screw cap digestion vessels

6.6 Auto-pipetters, various volumes

6.7 Ultra-pure deionized (DI) water (>16.3 MΩ)

6.8 Nitric Acid (HNO_3) – concentrated, optima grade

6.9 Hydrochloric Acid (HCl) – concentrated, optima grade

6.10 Appropriate purchased traceable single element stock standards

6.11 Calibration Stock Standards – various concentration levels, SCP Science Custom Blends, or equivalent

6.12 Second Source Stock Standards – various concentration levels, Inorganic Ventures #LTS-CALQC-1, #LTS-CALQC-2, and #LTS-CALQC-3, or equivalent

6.13 ICP-MS Internal Standard - 10 ppb lithium, bismuth, indium, scandium, terbium and yttrium solution

6.14 Interference standards – ICSA and ICSAB – various concentration levels

6.15 Liquid Argon doers

7. PROCEDURE

7.1 Preparation of Samples

7.1.1 Samples are prepped for analysis by using the SOP entitled 'Preparation of Samples for Testing by ICP-MS'.

7.2 Calibration

7.2.1 Refer to Equipment SOP entitled 'Inductively Coupled Plasma – Mass Spectroscopy' for instrument set-up.

7.2.2 The calibration consists of three calibration standard prepared in 1% HNO_3 from the Calibration Stock Standards and a calibration blank. An example of the calibration level would be:

Standard 1

Element/Mass	Level (ppb)	Element/Mass	Level (ppb)	Element/Mass	Level (ppb)
Be 9	0.50	Mn 55	0.50	Ag 107	0.50
Na 23	2.5	Fe 56	2.5	Cd 114	0.50
Mg 24	2.5	Co 59	0.50	Sn 118	0.50
Al 27	2.5	Ni 60	0.50	Sb 121	0.50
K 39	2.5	Cu 63	0.50	Ba 137	0.50
Ca 44	2.5	Zn 66	2.5	Tl 205	0.50
Ti 49	0.50	As 75	0.50	Pb (206 207,208)	0.50
V 51	0.50	Se 78	0.50		
Cr 52	0.50	Mo 98	0.50	U 238	0.50

Standard 2

Element/Mass	Level (ppb)	Element/Mass	Level (ppb)	Element/Mass	Level (ppb)
Be 9	10	Mn 55	10	Ag 107	10
Na 23	50	Fe 56	50	Cd 114	10
Mg 24	50	Co 59	10	Sn 118	10
Al 27	50	Ni 60	10	Sb 121	10
K 39	50	Cu 63	10	Ba 137	10
Ca 44	50	Zn 66	50	Tl 205	10
Ti 49	10	As 75	10	Pb (206 207,208)	10
V 51	10	Se 78	10		
Cr 52	10	Mo 98	10	U 238	10

Standard 3

Element/Mass	Level (ppb)	Element/Mass	Level (ppb)	Element/Mass	Level (ppb)
Be 9	40	Mn 55	40	Ag 107	40
Na 23	200	Fe 56	200	Cd 114	40
Mg 24	200	Co 59	40	Sn 118	40
Al 27	200	Ni 60	40	Sb 121	40
K 39	200	Cu 63	40	Ba 137	40
Ca 44	200	Zn 66	200	Tl 205	40
Ti 49	40	As 75	40	Pb (206 207,208)	40
V 51	40	Se 78	40		
Cr 52	40	Mo 98	40	U 238	40

7.2.3 Calibration curve calculations are found in the QA Manual.

7.2.4 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.3 Analysis

7.3.1 Standards required for each method's analysis are outlined below.

7.3.2 Method EPA 6020

7.3.2.1 Instrument Detection Limits (IDLs) – IDLs can be estimated by calculating the average of the standard deviation of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as if it was a separate analytical sample. IDLs must be determined every three months.

7.3.2.2 Initial Calibration Verification (ICV) – This is a multi-element standard in 1% HNO_3 prepared from the Second Source Stock Standards and is also known as the Calibration Verification Standard (CVS). It is analyzed following the calibration and must recover within ± 10% of the true value. No data for failing masses can be reported.

7.3.2.3 Initial Calibration Blank (ICB) – This is the Calibration Blank, a 1% HNO_3 solution in DI water. It is analyzed following the ICV at the beginning of the run. For elements of interest, the absolute value of the result must be less than 3 times the current IDL. No data for failing masses can be reported.

7.3.2.4 Continuing Calibration Verification (CCV) – This is a multi-element, mid-level standard in 1% HNO_3 prepared from the Calibration Stock Standards. It is analyzed at the beginning of each run, after every 10 samples, and at the end of the run. Elements of interest must recover within ± 10% of the true value. If not, samples bracketed by an out-of-spec CCV must be re-analyzed.

7.3.2.5 Continuing Calibration Blank (CCB) – This is the Calibration Blank, a 1% HNO_3 solution in DI water. It is analyzed following the CCV at the beginning of the run, after every 10 samples, and at the end of the run. For elements of interest, the absolute value of the result must be less than 3 times the current IDL. If not, samples bracketed by an out-of-spec CCB must be re-analyzed.

7.3.2.6 Interference Check Solution A (ICSA) and Interference Check Solution AB (ICSAB) – The ICSA and ICSAB are multi-element standards in 1% HNO_3 that measure the molecular-ion isobaric interferences and the adequacy of applied corrections. These standards need to be analyzed at the beginning of each run and/or every 12 hours during the run.

7.3.2.7 Linear Dynamic Range (LDR) Determination – The LDR must be determined annually or when a new method is developed. Standards are measured at successive levels with the criteria being that the standards recover within ± 10% of the true value. Samples outside the LDR are diluted and re-analyzed.

7.3.3 Method EPA 200.8

7.3.3.1 Instrument Detection Limits (IDLs) – IDLs can be estimated by calculating the average of the standard deviation of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as if it was a separate analytical sample. IDLs must be determined every three months.

7.3.3.2 Initial Calibration Verification (ICV) – This is a multi-element standard in 1% HNO_3 prepared from the Second Source Stock Standards and is also known as the Quality Control Standard (QCS). It is analyzed following the calibration and must recover within ± 10% of the true value. No data for failing masses can be reported.

7.3.3.3 Initial Calibration Blank (ICB) – This is the Calibration Blank, a 1% HNO_3 solution in DI water. It is analyzed following the ICV at the beginning of the run. For elements of interest, the absolute value of the result must be less than 3 times the current IDL. No data for failing masses can be reported.

7.3.3.4 Continuing Calibration Verification (CCV) – This is a multi-element, mid-level standard in 1% HNO_3 prepared from the Calibration Stock Standards. It is analyzed at the beginning of each run, after every 10 samples, and at the end of the run. The first CCV must recover within ± 10% of the true value. No data for failing masses can be reported. Continuing CCV determinations must recover within ±15% of true value. Samples bracketed by an out-of-spec CCV must be re-analyzed.

7.3.3.5 Continuing Calibration Blank (CCB) – This is the Calibration Blank, a 1% HNO_3 solution in DI water. It is analyzed following the CCV at the beginning of the run, after every 10 samples, and at the end of the run. For elements of interest, the absolute value of the result must be less than 3 times the current IDL. If not, samples bracketed by an out-of-spec CCB must be re-analyzed.

7.3.3.6 Interference Check Solution A (ICSA) and Interference Check Solution AB (ICSAB) – The ICSA and ICSAB are multi-element standards in 1% HNO_3 that measure the molecular-ion isobaric interferences and the adequacy of applied corrections. These standards need to be analyzed at the beginning of each run and/or every 12 hours during the run.

7.3.3.7 Linear Dynamic Range (LDR) Determination – The LDR must be determined annually or when a new method is developed. Standards are measured at successive levels with the criteria being that the standards recover within ± 10% of the true value. Samples outside the LDR are diluted and re-analyzed.

7.3.4 Samples with an in-solution concentration greater than the calibration level for an analyte of interest must be diluted such that the result falls below the calibration concentration if possible. If not, data must be flagged and qualified.

7.3.5 Export 'in solution' data for the run into LIMS.

7.4 Calculation

7.4.1 The concentration of the analyte in the sample is calculated using the following equations:

$$\text{Water Concentration } (mg/L) = \frac{(C_{in})(FV)(D)}{V}$$

$$\text{Soil Concentration } (mg/kg) = \frac{(C_{in})(FV)(D)}{M}$$

C_{in} = in-solution concentration, µg/mL
FV = final volume, mL
D = dilution factor
V = volume of sample, mL
M = mass of sample, g

7.5 Print a copy of the data from the LIMS for each project for internal validation.

7.6 Sign and date the data sheets.

7.7 Submit data sheets and raw data to a qualified Chemist for peer review. Peer reviewer signs and dates the data sheets after checking data for integrity as well as compliance to protocols.

7.8 Turn data sheet into the Client Manager.

7.9 Archive paper copy of raw data in Inorganic Daily Files.

7.10 Electronic copies of the raw data are stored on the network.

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

8.2 Retain samples for two months after the prep date.

8.3 Highly contaminated samples are returned to the client for disposal.

8.4 Samples and digestates are disposed of in the acid neutralizing laboratory sinks.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, on an annual basis. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. When the method blank result is 10% or more of the analyte concentration or is more than 2.2 times the analyte MDL, whichever is greater, the sample batch is redigested if possible. If it is not possible to redigest, the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Accuracy control limits are set at the following:

9.3.1.1 EPA 200.8 LCS = 85.0-115%.

9.3.1.2 EPA 6020 LCS = 80.0-120%.

9.3.1.3 EPA 200.8 and 6020 MS = 75.0-125%.

9.3.2 Precision control limits are set at $\leq$ 20% RPD.

9.3.3 QC calculations are found in the QA Manual

9.3.4 LCS and MS are reviewed.

9.3.5 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is re-digested if possible. If the batch cannot be re-digested, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.6 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS is flagged and/or a case narrative is written.

10. REPORTING

10.1 Soil samples results are reported in mg/kg on a dry weight basis.

10.2 Water sample results are reported in mg/L.

10.3 The reported result is rounded to two significant figures.

10.4 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

12. REFERENCES

12.1 EPA Method 200.8

12.2 EPA Method 6020

Appendix A

Initial Demonstration of Capability (IDC)
ICP-MS

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards of all the parameters and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual recoveries in concentration and %, the mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: EPA 200.8 = 85.0-115%, EPA 6020 = 80.0-120%
   Precision: $\leq$ 20% RPD

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the QA/QC Coordinator signs the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
ICP-MS

Parameter	Water MDL (µg/L)	Water RL (µg/L)	Soil MDL* (µg/kg)	Soil RL* (µg/kg)
Be 9	0.027	0.50	2.7	50
Ti 49	0.040	0.50	4.0	50
V 51	0.036	0.50	3.6	50
Cr 52	0.096	0.50	9.6	50
Mn 55	0.15	0.50	15	50
Co 59	0.0066	0.50	0.66	50
Ni 60	0.054	0.50	5.4	50
Cu 63	0.057	0.50	5.7	50
Zn 66	0.042	2.5	4.2	250
As 75	0.16	1.0	16	100
Se 78	0.24	1.0	24	100
Mo 98	0.047	0.50	4.7	50
Ag 107	0.067	0.50	6.7	50
Cd 114	0.017	0.50	1.7	50
Sn 118	0.042	0.50	4.2	50
Sb 121	0.046	0.50	4.6	50
Ba 137	0.10	0.50	10	50
Tl 205	0.0081	0.50	0.81	50
Pb (206,207,208)	0.032	0.50	3.2	50

*Note – Soil MDL and RL values do not take into consideration dilutions needed for high dissolved solid and chloride concentrations in soil digestions.

DOCUMENT REVIEW

DOCUMENT:	LABENV-066.1
REVIEWER:	Jaime Zwers
DATE:	08/28/08

SECTION	**CHANGES**
Cover Page	Updated to new form
1.1	Added "wastewater, non-potable water, solid and chemical materials"
3.1	Added "This SOP is applicable to aqueous samples or digestates of various matrices"
6.13	Added "ICP-MS Internal Standard - 10 ppb lithium, bismuth, indium, scandium, terbium and yttrium solution"
6.15	Added "Liquid Argon Dewars"
7.2.2	Replaced "one" with "three" and added new calibration standard tables
7.2.2	5-fold increase in zinc standard concentrations
Appendix B	Updated MDLs

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: PREPARATION OF SAMPLES FOR TESTING BY ICP-MS

SOP NO.: LABENV-065.3

Original Information		
Prepared by:	Cynthia Schultz	Date: 05/08/07
Technical Review:	Jaime Zwers	Date: 05/08/07
QA/QC Coordinator:	Lisa Bloomgren	Date: 05/08/07
Authorized by:	Cheryl Sykora	Date: 05/08/07

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Revised by:	Tammika Shedd	Date: 05/05/09
Signature:	______________________	Date: __________
Technical Review:	Viktor Yakovlev	Date: 04/30/09
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 05/11/09
Signature:	______________________	Date: __________

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FORM GEN-021 (05/07)

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: PREPARATION OF SAMPLES FOR TESTING BY ICP-MS
SOP NO.: LABENV-065.3

Original Information		
Prepared by:	Cynthia Schultz	Date: 05/08/07
Technical Review:	Jaime Zwers	Date: 05/08/07
QA/QC Coordinator:	Lisa Bloomgren	Date: 05/08/07
Authorized by:	Cheryl Sykora	Date: 05/08/07

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Revised by:	Tammika Shedd	Date:
Signature:	[signature]	Date: 05/05/09
Technical Review:	Viktor Yakovlev	Date:
Signature:	[signature]	Date: 4/30/09
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 5/11/09

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FORM GEN-021 (05/07)

SOP TITLE: PREPARATION OF SAMPLES FOR TESTING BY ICP-MS

1. PURPOSE

1.1 This document defines the preparation of samples prior to analysis by ICP-MS. The SOP is applicable to samples typically analyzed by EPA Methods 200.8 and 6020.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the SOP.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 The method is applicable to routine, homogenous water and soil samples.

3.2 Sample digests containing more than 0.2% solids may cause interference by blocking the nebulizer flow or plugging the cones. The digests should be diluted prior to analysis.

3.3 Samples with high in-solution element concentrations must be diluted prior to analysis to avoid damaging the instrument's detector.

3.4 If the laboratory will be filtering the sample for dissolved metals analyses, do not perform nitric acid preservation.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 Safety glasses and gloves should be worn when handling samples and reagents.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Water samples should be collected in polyethylene or glass containers and preserved with 1:1 nitric acid to a pH < 2 unless filtration is to be performed in the laboratory for dissolved metals analysis. Samples requiring dissolved metals analysis need to be filtered through a 0.45 µm filter prior to the preservation with 1:1 nitric acid.

5.4 If a water sample is received with pH > 2 and does not require filtration by the laboratory, it is preserved in the laboratory and allowed to sit for a minimum of 24 hours at which time the pH is re-tested. If pH < 2, proceed. If not, repeat until pH is < 2, if possible. Highly alkaline samples may need to be digested at a reduced volume with excess acid, rather than diluting the original sample in an attempt to lower the pH.

5.5 Document the final pH of all samples in the Digestion Log Book under “Comments.”

5.6 Soil samples should be collected in polyethylene or glass containers and stored at 4 ± 2 ºC.

5.7 The recommended holding time for water and soil samples is six months.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 Block digester

6.2 Screw cap digestion vessels

6.3 Plastic watch glasses

6.4 Nitric acid (HNO_3) (Optima grade)

6.5 Hydrochloric Acid (HCl) (Optima grade)

6.6 Centrifuge

6.7 Ultra-pure deionized (DI) water (>16.3 MΩ)

6.8 Appropriate spiking standards, SCP Science Custom Blends, or equivalent

6.9 Auto-pipetters, various volumes

6.10 Top loading balance – capable of reading 0.01 g

7. PROCEDURE

7.1 Preparation of Water Samples

7.1.1 Fill out the appropriate information in the Digestion Log Book, including sample numbers to be prepared. Confirm sample ID and requested analyte information with the Chain-of-Custody (c-o-c).

7.1.2 For Quality Control (QC), indicate the prep batch # under the sample ID for the Blank, Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD). The LCS is also referred to as the Laboratory Fortified Blank (LFB) or Blank Spike (BS). The prep batch number is obtained from LIMS.

7.1.3 Label digestion vessels with sample IDs. Label digestion vessels for the Blank, LCS, and LCSD including the batch number. Along with the sample ID, label MS for sample matrix spike and MSD for sample matrix spike duplicate. MS is also referred to as the Laboratory Fortified Matrix (LFM).

7.1.4 Shake all samples prior to transferring into digestion vessels.

7.1.5 Measure out 50 mL of DI water for each of the Blank, LCS, and LCSD using graduations on the digestion vessels.

7.1.6 Measure out 50 mL of each sample into its assigned digestion vessel. Measure directly into digestion vessels using the graduations on the side of the vessels. Graduation marks are certified for volume. Records are kept in the QA/QC department.

7.1.7 For one of the water samples, measure out two additional aliquots, one for the MS and one for the MSD.

7.1.8 Alternate volumes may be used if sample is limited or a dilution is required.

7.1.9 Record the initial volumes of all samples in the Digestion Log Book and LIMS.

7.1.10 Measure out up to 20 samples per batch. If less than 20 samples are measured, “Z” out remaining spaces in the Digestion Log Book, initial, and date.

7.1.11 Transfer the samples to a rack. Order the samples in the rack from left to right on the long row as they appear in the Digestion Log Book. The labels for the LCS, LCSD, MS and MSD are seen in the first row.

7.1.12 A typical spike list is given in the table below. Add 0.050 mL for each of the three groups listed below to the LCS, LCSD, MS, and MSD (final volume is 50 mL). Record all information in the Digestion Log Book and LIMS.

Parameter	**Stock Concentration (ppm)**	**Final Concentration (ppm)**
Tin	20	0.020
Antimony	20	0.020
Arsenic	20	0.020
Barium	20	0.020
Beryllium	20	0.020
Cadmium	20	0.020
Chromium	20	0.020
Cobalt	20	0.020
Copper	20	0.020
Lead	20	0.020
Manganese	20	0.020
Molybdenum	20	0.020
Nickel	20	0.020
Selenium	20	0.020
Silver	20	0.020
Thallium	20	0.020
Titanium	20	0.020

Parameter	Stock Concentration (ppm)	Final Concentration (ppm)
Uranium	20	0.020
Vanadium	20	0.020
Zinc	20	0.020
Aluminum	100	0.10
Calcium	100	0.10
Iron	100	0.10
Magnesium	100	0.10
Potassium	100	0.10
Sodium	100	0.10

7.1.13 Add 0.5 mL nitric acid to all the samples (including Blank, LCS, and LCSD).

7.1.14 If analyzing for tin or silver, a separate digestion is needed with 0.5 mL nitric acid and 1.0 mL hydrochloric acid.

7.1.15 Record the acid added in the Digestion Log Book.

7.1.16 Ensure the block digester temperature meter reads 120 °C. (Note: This is the temperature of the block coil, actual sample temperature is approximately 95-97 °C).

7.1.17 Transfer racks of samples to the block digester and place plastic watch glasses over each digestion vessel. Record the time in the Digestion Log Book.

7.1.18 Let samples heat for 2 to 3 hours, ensuring sufficient volume loss.

7.1.19 Remove samples from block digester and record the time in the Digestion Log Book. Allow samples to cool.

7.1.20 Bring all samples up to 50 mL with DI water using the graduations on the digestion vessels.

7.1.21 Record the final volumes in the Digestion Log Book and LIMS.

7.1.22 Cap all samples.

7.1.23 Place samples in batch holders in the order that they are listed in the Digestion Log Book.

7.1.24 If particulates are present in the sample, allow solids to settle out. A centrifuge may be used for this purpose. Carefully decant off an aliquot for analysis.

7.2 Preparation of Soil Samples

7.2.1 Fill out the appropriate information in the Digestion Log Book, including sample numbers to be prepared. Confirm sample ID and requested analyte information with the Chain-of-Custody (c-o-c).

7.2.2 For Quality Control (QC), indicate the prep batch # under the sample ID for the Blank, Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD). The LCS is also referred to as the Laboratory Fortified Blank (LFB) or Blank Spike (BS). The prep batch number is obtained from LIMS.

7.2.3 Label digestion vessels with sample IDs. Label digestion vessels for the Blank, LCS, and LCSD including the batch number. Along with the sample ID, label MS for sample matrix spike and MSD for sample matrix spike duplicate. MS is also referred to as the Laboratory Fortified Matrix (LFM).

7.2.4 Weigh out 0.50 g of the well-mixed soil sample into a clean, labeled digestion vessel. It may occasionally be necessary to alter the weight of a sample due to limited availability of sample or the need to achieve lower detection levels. For one of the soil samples, weigh out two additional aliquots, one for the MS and one for the MSD.

7.2.5 Record the weights of all samples in the Digestion Log Book and LIMS.

7.2.6 Weigh out up to 20 samples per batch. If less than 20 samples are weighed, “Z” out remaining spaces in the Digestion Log Book, initial, and date.

7.2.7 Transfer the samples to a rack. Order the samples in the rack from left to right on the long row as they appear in the Digestion Log Book. The labels for the LCS, LCSD, MS and MSD are seen in the first row.

7.2.8 A typical spike list is given in the table below. Add 0.05 mL for each of the three groups listed below to the LCS, LCSD, MS, and MSD (final volume is 50 mL). Record all information in the Digestion Log Book and LIMS.

Parameter	**Stock Concentration (ppm)**	**Final Concentration (ppm)**
Tin	20	0.020
Antimony	20	0.020
Arsenic	20	0.020
Barium	20	0.020
Beryllium	20	0.020
Cadmium	20	0.020
Chromium	20	0.020
Cobalt	20	0.020
Copper	20	0.020
Lead	20	0.020
Manganese	20	0.020
Molybdenum	20	0.020
Nickel	20	0.020
Selenium	20	0.020
Silver	20	0.020
Thallium	20	0.020
Titanium	20	0.020
Uranium	20	0.020
Vanadium	20	0.020
Zinc	20	0.020

Parameter	Stock Concentration (ppm)	Final Concentration (ppm)
Aluminum	100	0.10
Calcium	100	0.10
Iron	100	0.10
Magnesium	100	0.10
Potassium	100	0.10
Sodium	100	0.10

7.2.9 Add 5 mL DI water, 1 mL nitric acid, and 1.25 mL hydrochloric acid to all of the digestion vessels.

7.2.10 Ensure the block digester temperature meter reads 120 °C. (Note: This is the temperature of the block coil, actual sample temperature is approximately 95-97 °C).

7.2.11 Transfer racks of samples to the block digester and place plastic watch glasses over each digestion vessel. Record the time in the Digestion Log Book.

7.2.12 Allow samples to reflux for 30 minutes.

7.2.13 Remove the samples from the block digester and allow the samples to cool. Record the time in the Digestion Log Book.

7.2.14 Bring all samples up to 50 mL with DI water using the graduations on the digestion vessels.

7.2.15 Record the final volumes in the Digestion Log Book and LIMS.

7.2.16 Allow solids to settle out by either centrifuge or sitting over night.

7.2.17 The sample digests need to be diluted prior to analysis to adjust the chloride and dissolved solids concentrations. Dilute a 10 mL aliquot of the sample digest with DI water to a 50 mL final volume. Record the dilution in the Digestion Log Book.

7.3 Calibration, analysis and calculation are not applicable to this SOP but are addressed in the appropriate analytical SOP.

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

9. QA/QC

9.1 Follow the QA/QC protocol outlined in the appropriate analytical SOP.

10. REPORTING

Not applicable

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

12. REFERENCES

12.1 EPA Method 200.8

12.2 EPA Method 6020

Appendix A

Initial Demonstration of Capability (IDC)
Preparation of Samples for ICP-MS

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards of all the parameters in lab-grade water and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: 200.8 = 85.0-115%, 6020 = 80.0-120% (200.8/6020 may be combined if tighter limits are used for acceptance)
   Precision: 200.8/6020= ≤ 20 % RPD

7. The reagent blank must be less than the reporting limit (RL).

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

DOCUMENT REVIEW

DOCUMENT:	SOP LABENV-065.3
REVIEWER:	Tammika Shedd
DATE:	03/26/09

SECTION	**CHANGE**	**RATIONALE**
Document Review	Updated form	Revised form

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

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SOP NO.: LABENV-053.6

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Prepared by:	Lisa Bloomgren	Date: 01/15/02
Technical Review:		Date:
QA/QC Coordinator:	Terri A. Olson	Date: 04/26/02
Authorized by:	Cheryl Sykora	Date: 05/22/02

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Signature:	______________________	Date: __________
Technical Review:	Cynthia Schultz	Date: 04/03/08
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 04/04/08
Signature:	______________________	Date: __________

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LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: MERCURY ANALYSIS BY COLD VAPOR GENERATION
SOP NO.: LABENV-053.6

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Signature:	______________________	Date: __________
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Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 4/04/08

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FORM GEN-021 (05/07)

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

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Revised by:	Jaime Zwers	Date:
Signature:	Jaime Zwers	Date: 4/3/08
Technical Review:	Cynthia Schultz	Date:
Signature:	[signature]	Date: 4/3/08
Authorized by:	Cheryl Sykora	Date:
Signature:		Date:

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FORM GEN-021 (05/07)

SOP TITLE: MERCURY ANALYSIS BY COLD VAPOR GENERATION

1. PURPOSE

1.1 This document defines the procedure to be followed for analyzing samples for mercury by cold vapor technique using an automated atomic absorption spectrophotometer. The SOP is applicable to samples analyzed by EPA 245.1, EPA 7470A, and EPA 7471A.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the SOP.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 Samples may need to be run at a dilution if they exceed the calibration or their matrices interfere with analysis.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 Safety glasses and gloves should be worn when handling samples and reagents.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Water samples should be collected in polyethylene or glass containers, preserved with 1:1 nitric acid to a pH < 2.

5.4 If a water sample is received with pH > 2, it is preserved in the laboratory and allowed to sit for a minimum of 24 hours at which time the pH is re-tested. The addition of the acid is noted on the appropriate chain-of-custody. If pH < 2, proceed. If not, repeat until pH is < 2, if possible. Highly alkaline samples may need to be digested at a reduced volume with excess acid, rather than dilute the original sample in an attempt to lower the pH.

5.5 Document the final pH of all samples in the Digestion Log Book under "Comments."

5.6 The recommended holding time for water samples is 28 days.

5.7 Solid samples should be collected in polyethylene or glass containers and stored at 4 ± 2 °C.

5.8 The recommended holding time for solid samples is 28 days.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 CETAC M6000 Mercury Analyzer equipped with naphion cartridge, or equivalent

6.2 ASX-500 Model 510 autosampler, or equivalent

6.3 Top loading balance

6.4 Digestion vessels

6.5 Hydrochloric acid (HCl), concentrated, trace metal grade

6.6 Stannous chloride, reagent grade

6.7 Stannous chloride reducing solvent (10%) in 7% HCl - add 25 g of stannous chloride to a 250 mL volumetric flask containing 100 mL of DI water and 17.5 mL of HCl, dilute to volume with DI water, and invert repeatedly until stannous chloride is in solution (uncap periodically to vent gas)

6.8 Nitric acid (HNO_3), concentrated, trace metal grade

6.9 Aqua regia (3:1 HCl:HNO_3 solution) – prepare immediately before use

6.10 Potassium permanganate solution (5%)

6.11 Hydroxylamine hydrochloride, reagent grade

6.12 Certified Calibration Stock Standard – 1000 ppm (two different lots numbers are used)

6.13 Intermediate Stock Standard 1 (ISS1) – dilute 2.5 mL of the 1000 ppm certified stock standard (first lot number) and 12.5 mL of Aqua Regia with DI water in a 250 mL volumetric flask to produce a 10 ppm solution

6.14 Intermediate Stock Standard 2 (ISS2) – dilute 2.5 mL of the 1000 ppm certified stock standard (second lot number) and 12.5 mL of Aqua Regia with DI water in a 250 mL volumetric flask to produce a 10 ppm solution

6.15 Mercury Working Standard Solution 1 (MWSS1) – dilute 5.0 mL of ISS1 and 25 mL of Aqua Regia with DI water in a 500 mL volumetric flask to produce a 0.10 ppm solution and use this solution for calibration, LCS, LCSD, MS, and MSD – the spike concentration for the LCS, LCSD, MS, and MSD is 2.0 ppb

6.16 Mercury Working Standard Solution 2 (MWSS2) – dilute 5.0 mL of ISS2 and 25 mL of Aqua Regia with DI water in a 500 mL volumetric flask to produce a 0.10 ppm solution and use this solution for the QC standard or second source – the concentration for the second source standard is 5.0 ppb

7. PROCEDURE

7.1 Calibration

7.1.1 Prepare calibration standards in digestion vessels at a minimum of 3 concentration levels, ranging from 0.20 – 10 ppb, by diluting MWSS1 with DI water to the 50 mL graduation. A typical calibration curve would be:

MWSS1 mL/50 mL	Conc. (ppb)
0.0	0.0
0.10	0.20
0.25	0.50
1.0	2.0
2.5	5.0
5.0	10

7.1.2 Prepare the QC standard, or second source, in a digestion vessel by diluting 2.5 mL of MWSS2, with DI water, to the 50 mL graduation.

7.1.3 Using a disposable pipet, add 2.5 mL of aqua regia to all the digestion vessels.

7.1.4 Add 5.0 mL of 5% potassium permanganate solution to each vessel.

7.1.5 Add approximately 400 mg (~½ inch back on tip of spatula) of hydroxylamine hydrochloride to reduce the potassium permanganate, cap tightly and mix.

7.1.6 The calibration curve is Concentration vs. Response. Correlation Coefficients should be 0.995 or greater.

7.1.7 Calibration curve calculations are found in the QA Manual.

7.1.8 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.2 Analysis

7.2.1 Fill out the Mercury Log Book.

7.2.2 The QC standard, or second source, is used as the Initial Calibration Verification (ICV) and the Continuing Calibration Verification (CCV).

7.2.3 The QC standard, followed by a QC blank, should be run at the beginning of the run (ICV), after every ten samples (CCV) and at the end of the run.

7.2.4 For Methods EPA 7470A and EPA 7471A, the ICV and CCV (QC standards) recovery range is 90.0-110%. For Method EPA 245.1, the ICV recovery range is 95.0-105% and the CCV recovery range is 90.0-110%. If the CCV standard fails, the samples bracketed with that standard must be reanalyzed.

7.2.5 The absolute value of the QC blank must be less than the Reporting Limit (RL). If the QC blank fails, the samples bracketed with that blank have to be reanalyzed.

7.2.6 Set up the auto sampler as follows:

7.2.6.1 Place calibration blank, standards, and second source in the standards rack.

7.2.6.2 Place samples, spikes, and batch blank in autosampler racks.

7.2.7 Check instrument waste container level and dispose appropriately if full.

7.2.8 Make sure tubing is fitted correctly for sample and reagent lines. Replace if needed.

7.2.9 Check the lamp current and replace the lamp when the current reaches 13-14 mA.

7.2.10 Check the gas-liquid separator, inlet and drain tube for deposits. If deposits are found, clean with a 50% nitric acid solution and rinse thoroughly with DI.

7.2.11 Analyze calibration standards and samples.

7.2.12 Upon completion of the automated run, complete filling out the mercury logbook.

7.3 Calculation

7.3.1 Compute the concentration of the analyte in the sample using the following equation:

$$Water\ Concentration\ (mg/L) = \frac{(C_{in})(FV)(D)}{V(1000)}$$

$$Soil\ Concentration\ (mg/kg) = \frac{(C_{in})(FV)(D)}{M(1000)}$$

C_{in} = in-solution concentration, µg/L
FV = final volume, mL
D = dilution factor
V = volume of sample, mL
M = mass of sample, g

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

8.2 Acidic waste must be neutralized prior to disposal.

8.3 Highly contaminated samples are returned to the client for disposal.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, on an annual basis. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDL and RL values can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each group of up to 20 samples prepared at the same time. The absolute value of the method blank must be less than the reporting limit or the sample batch is re-digested, if possible. If it is not possible to re-digest, the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Method limits are used for compliance (see Appendix C).

9.3.2 QC calculations are found in the QA Manual.

9.3.3 LCS and MS are reviewed.

9.3.4 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is re-digested if possible. If the batch cannot be re-digested, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.5 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS is flagged and/or a case narrative is written.

10. REPORTING

10.1 Solid sample results are reported in mg/kg on a dry weight basis.

10.2 Bulk sample results are reported in mg/kg on an as received basis.

10.3 Water sample results are reported in mg/L.

10.4 The reported result is rounded to two significant figures.

10.5 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A - Initial Demonstration of Capability

11.2 Appendix B - Method Detection Limits and Report Limits

11.3 Appendix C - Method Limits

12. REFERENCES

12.1 EPA Methods 245.1, 7470A and 7471A

12.2 M-6000A Mercury Analyzer Operator's Manual, CETAC Technologies, Inc., 480035, Version 1.2, March, 1997

12.3 M-6000A Mercury Analyzer Software Manual, CETAC Technologies, Inc., 480034, Version 1.1, May, 1997

12.4 ASX-500 Model 510 Auto Sampler Operator's Manual, CETAC Technologies, Inc., 480049, Version 1.0, March, 1997

Appendix A

Initial Demonstration of Capability (IDC)
Mercury Analysis by Cold Vapor Generation

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form ‘IDC 4 rep with RPD’, the individual recoveries in concentration and %, the mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: EPA 245.1 = 85.0-115%, EPA 7470A and 7471A = 80.0-120%
   (245.1/7470A may be combined if tighter limits are used for acceptance)
   Precision: $\leq$ 20.0% RPD

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the QA/QC Coordinator signs the form and a copy of the form is placed in the employee’s personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
Mercury Analysis by Cold Vapor Generation

Water

Parameter	MDL (mg/L)	RL (mg/L)
Mercury	0.000031	0.00020

Soil

Parameter	MDL (mg/kg)	RL (mg/kg)
Mercury	0.0031	0.10

Appendix C

Limits for Mercury Analysis by Cold Vapor Generation

Method	Accuracy Method Limits (%)	Precision Method Limits (%RPD)
EPA 245.1 (LCS)	85.0-115	$\leq$ 20
EPA 245.1 (MS)	75.0-125	$\leq$ 20
7470A (LCS)	80.0-120	$\leq$ 20
7470A (MS)	75.0-125	$\leq$ 20
7471A (LCS)	80.0-120	$\leq$ 20
7471A (MS)	75.0-125	$\leq$ 20

DOCUMENT REVIEW

DOCUMENT:	LABENV-053.6
REVIEWER:	Jaime Zwers
DATE:	04/03/08

SECTION	**CHANGES**
Cover Page	Updated to new form
9.3	Deleted sections regarding generation of inhouse control limits
Appendix B	Updated MDLs

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: TOTAL ORGANIC CARBON

SOP NO.: LABENV-045.5

Original Information		
Prepared by:	Brian Leigh	Date: 03/15/01
Technical Review:		Date:
QA/QC Coordinator:	Terri A. Olson	Date: 11/07/01
Authorized by:	Cheryl Sykora	Date: 11/12/01

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Signature:	______________________	Date: __________
Technical Review:	Jaime Zwers	Date: 04/02/08
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 04/04/08
Signature:	______________________	Date: __________

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LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: TOTAL ORGANIC CARBON
SOP NO.: LABENV-045.5

Original Information		
Prepared by:	Brian Leigh	Date: 03/15/01
Technical Review:		Date:
QA/QC Coordinator:	Terri A. Olson	Date: 11/07/01
Authorized by:	Cheryl Sykora	Date: 11/12/01

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Supersedes:	LABENV-045.4	Date: 04/19/07
Revised by:	Cynthia Schultz	Date:
Signature:	______________________	Date: __________
Technical Review:	Jaime Zwers	Date:
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 4/04/08

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LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: TOTAL ORGANIC CARBON
SOP NO.: LABENV-045.5

Original Information		
Prepared by:	Brian Leigh	Date: 03/15/01
Technical Review:		Date:
QA/QC Coordinator:	Terri A. Olson	Date: 11/07/01
Authorized by:	Cheryl Sykora	Date: 11/12/01

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Signature:	[signature]	Date: 4/2/08
Technical Review:	Jaime Zwers	Date:
Signature:	[signature]	Date: 4/2/08
Authorized by:	Cheryl Sykora	Date:
Signature:		Date:

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FORM GEN-021 (05/07)

SOP TITLE: TOTAL ORGANIC CARBON

1. PURPOSE

1.1 This document defines the procedure to be followed for determining total organic carbon (TOC) in aqueous samples. Organic carbon is converted to CO_2 by wet chemical oxidation. An Infrared (IR) detector measures the CO_2 formed. The SOP is applicable to samples typically analyzed by Standard Methods (SM) 5310 C, Online Version, 2000.

1.2 This SOP may also be used for dissolved organic carbon analysis if the sample was filtered with a 0.45 µm filter prior to preservation.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the standard operating procedure.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This method is applicable to aqueous samples only.

3.2 Inorganic carbon interferes with organic carbon analysis. The inorganic carbon is removed with phosphoric acid and nitrogen gas.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 A lab coat and safety glasses should be worn.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Samples should be collected in glass containers and preserved with H_2SO_4 to a pH < 2 and stored at 4 ± 2 °C.

5.4 The recommended holding time for water samples is 28 days.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 O.I. Analytical Model 700 TOC Analyzer, or equivalent

6.2 Balance, capable of reading 0.01 g

6.3 Analytical balance, capable of reading 0.1 mg

6.4 Volumetric flasks

6.5 Serological pipettes

6.6 Reagent water – distilled or deionized water containing TOC < 200 ppb carbon

6.7 Potassium Acid Phthalate (KHP), ACS Primary Standard Grade (two different lots numbers are used)

6.8 Sodium persulfate ($Na_2S_2O_8$), 100% - ACS grade, or equivalent

6.9 Phosphoric acid (H_3PO_4), 85% - ACS grade, or equivalent

6.10 TOC Calibration Stock Solution - dilute 0.213 g of the 100% KHP (first lot number) into a 100 mL volumetric flask with reagent water to produce a 1,000 µg/mL TOC Calibration Stock Solution

6.11 TOC Second Source Stock Solution - dilute 0.213 g of the 100% KHP (second lot number) into a 100 mL volumetric flask with reagent water to produce a 1,000 µg/mL TOC Second Source Stock Solution

6.12 TOC Calibration Standard – dilute 2.5 mL of the 1,000 µg/mL TOC Calibration Stock Solution into a 100 mL volumetric flask with reagent water to produce a 25 µg/mL TOC Calibration Standard

6.13 TOC Calibration Verification Standard (CVS) – dilute 2.5 mL of the 1,000 µg/mL TOC Second Source Stock Solution into a 100 mL volumetric flask with reagent water to produce a 25 µg/mL TOC ICV Standard

6.14 Sodium persulfate ($Na_2S_2O_8$) (100 g/L) - dissolve 25 g $Na_2S_2O_8$ into 250 mL of reagent water, stirring if necessary, but not heating (prior to use, purge any residual CO_2 from the $Na_2S_2O_8$ solution by transferring the solution into the proper reagent bottle, placing in a microwave oven, heating until the solution just comes to a boil, then tightening the lid on the reagent bottle and cooling in cold water)

6.15 Phosphoric acid (5%) - dilute 5.9 mL of the 85% H_3PO_4 into a 100 mL volumetric flask with reagent water to produce a 5% solution

7. PROCEDURE

7.1 Calibration

7.1.1 Begin purging the TOC analyzer with nitrogen the day before analysis is to begin.

7.1.2 Drain any sodium persulfate from the analyzer and reagent bottle and refill with fresh solution.

7.1.3 Check that the analyzer's 5% phosphoric acid level is sufficient, and add if needed.

7.1.4 Connect reagent lines to the appropriate reagent bottles and prime both lines. Place sample line in fresh de-ionized water and continuously run water until stable baseline in millivolts for blank is attained. Average the last three replicates for calibration.

7.1.5 Run 2-3 replicates of the TOC Calibration Standard.

7.1.6 Select the TOC calibration mode and enter the mean value in millivolts for the TOC Blank and TOC Calibration Standard.

7.1.7 Analyze a continuing calibration blank (CCB) at the beginning of the batch, after every ten samples and at the end of the batch. The result must be less than the reporting limit.

7.1.8 Run a Calibration Verification Standard (CVS) immediately following the CCB at the beginning of the batch, after every ten samples, and at the end of the batch. If the result of this standard is not within 80.0-120% recovery, the instrument should be recalibrated.

7.1.9 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum by analyzing a standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit.

7.2 Analysis

7.2.1 Place the sample line in the sample container, load sample, and start run.

7.2.2 Allow analysis of each sample to complete before loading next sample. Repeat for each sample.

7.2.3 Analyze a sample duplicate for every 10 samples.

7.2.4 All results are recorded in the TOC laboratory notebook.

7.2.5 The IR detector has a linear range of 1000 millivolts, which equates to approximately 50 µg/mL sample concentration. Samples above this range should be diluted with de-ionized water and re-analyzed.

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures. Samples are retained for 30 days, then neutralized and dumped down normal laboratory sink.

8.2 Highly contaminated samples are returned to the client for disposal.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, on an annual basis. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. The method blank must be less than the reporting limit or the sample batch is re-analyzed if possible. If it is not possible to re-extract, the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Duplicate

9.3.1 One sample duplicate is to be analyzed per sample batch of 10 or fewer samples. The %RPD between sample and duplicate must be ≤ 20%.

9.3.2 QC calculations are found in the QA Manual

10. REPORTING

10.1 Results are reported in mg/L.

10.2 The reported result is rounded to two significant figures.

10.3 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

12. REFERENCES

12.1 Standard Methods for the Examination of Water and Wastewater, Method 5310 C, Online Version, 2000

12.2 Model 700 TOC Analyzer Operator Manual, OI Analytical PN 19649

Appendix A

Initial Demonstration of Capability (IDC)
Total Organic Carbon

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards in reagent water and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: 80.0-120%
   Precision: $\leq$ 20.0% RPD

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
Total Organic Carbon

Parameter	Water MDL (mg/L)	Water RL (mg/L)
Total Organic Carbon (TOC)	0.38	1.5

DOCUMENT REVIEW

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REVIEWER:	Cynthia Schultz
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Cover Page	Updated to new form
Appendix B	Updated MDL and RL

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

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Prepared by:	William R. Dahl	Date: 01/30/02
Technical Review:	Brian Leigh	Date: 02/26/02
QA/QC Coordinator:	Terri A. Olson	Date: 02/26/02
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Signature:	______________________	Date: __________
Technical Review:	Jaime Zwers	Date: 04/03/08
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 04/07/08
Signature:	______________________	Date: __________

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LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: PREPARATION OF SOLID SAMPLES FOR TESTING BY ICP OR FLAME AA

SOP NO.: LABENV-043.4

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Prepared by:	William R. Dahl	Date: 01/30/02
Technical Review:	Brian Leigh	Date: 02/26/02
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LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: PREPARATION OF SOLID SAMPLES FOR TESTING BY ICP OR FLAME AA

SOP NO.: LABENV-043.4

Original Information		
Prepared by:	William R. Dahl	Date: 01/30/02
Technical Review:	Brian Leigh	Date: 02/26/02
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Technical Review:	Jaime Zwers	Date: x
Signature:	Jaime Zwers	Date: 4/3/08
Authorized by:	Cheryl Sykora	Date: x
Signature:		Date:

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FORM GEN-021 (05/07)

SOP TITLE: PREPARATION OF SOLID SAMPLES FOR TESTING BY ICP OR FLAME AA

1. PURPOSE

1.1 This document defines the preparation of samples prior to analysis by ICP and/or Flame AA. The SOP is applicable to samples typically analyzed prepared by EPA Methods 3050B.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the standard operating procedure.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This method is applicable to all soil matrices, and will also apply to terminology referring to solids and sludges.

3.2 There are many materials that require specific method development to achieve desired objectives. These are handled on a case-by-case basis and may not be covered under this procedure.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 Safety glasses and gloves should be worn when handling samples and reagents.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample’s integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample’s integrity.

5.3 Solid samples should be collected in polyethylene or glass containers and stored at 4 ± 2 ºC.

5.4 The recommended holding time for soil samples is six months.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 Block digester

6.2 Screw cap digestion vessels

6.3 Plastic watch glasses

6.4 Nitric acid (HNO_3) 1:1 (trace metal grade:DI)

6.5 Hydrochloric Acid (HCl) 1:1 (trace metal grade:DI)

6.6 Plunge filters

6.7 Deionized (DI) water (>16.3 MΩ)

6.8 Top loading balance – capable of reading 0.01 g

7. PROCEDURE

7.1 Fill out the appropriate information in the Digestion Log Book, including sample numbers to be prepared. Confirm sample ID and requested analyte information with the Chain-of-Custody (c-o-c).

7.2 For Quality Control (QC), indicate the prep batch # under the sample ID for the Blank, Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD). The LCS is also referred to as the Laboratory Fortified Blank (LFB) or Blank Spike (BS). The prep batch number is obtained from LIMS.

7.3 Label digestion vessels with sample IDs. Label digestion vessels for the Blank, LCS, and LCSD including the batch number. Along with the sample ID, label MS for sample matrix spike and MSD for sample matrix spike duplicate. MS is also referred to as the Laboratory Fortified Matrix (LFM).

7.4 Weigh out between 1.00 and 1.04 g aliquot of soil and transfer to a pre-labeled digestion vessel. It may occasionally be necessary to alter the weight of a sample due to limited availability of sample or the need to achieve lower detection levels. For one of the solid samples, weigh out two additional aliquots, one for the MS and one for the MSD.

7.5 Record the weights of all samples in the Digestion Log Book and LIMS.

7.6 Weigh out up to 20 samples per batch. If less than 20 samples are measured, "Z" out remaining spaces in the Digestion Log Book, initial, and date.

7.7 Place the samples in a rack. Arrange them from left to right, on the long row, as they appear in the Digestion Log Book, thus placing the LCS, LCSD, MS and MSD in the first row for easy spiking.

7.8 A typical spike list is given in the table below. Add 0.10 mL for each of the three groups listed below to the LCS, LCSD, MS, and MSD (final volume is 50 mL). Record all information in the Digestion Log Book and LIMS.

Parameter	Stock Concentration (ppm)	Final Concentration (ppm)
Aluminum	2000	4.0
Barium	400	0.80
Calcium	4000	8.0
Cobalt	400	0.80
Iron	2000	4.0
Magnesium	4000	8.0
Manganese	400	0.80
Potassium	2000	4.0
Sodium	4000	8.0
Vanadium	400	0.80
Zinc	400	0.80
Arsenic	400	0.80
Beryllium	40	0.080
Cadmium	400	0.80
Chromium	400	0.80
Copper	400	0.80
Lead	400	0.80
Nickel	400	0.80
Selenium	400	0.80
Silver	40	0.080
Thallium	400	0.80
Antimony	400	0.80
Boron	400	0.80
Molybdenum	400	0.80
Tin	400	0.80

7.9 Add 4 mL of 1:1 HNO_3 and 5 mL of 1:1 HCl to all samples (including Blank, LCS, & LCSD).

7.10 Ensure the block digester temperature meter reads 125 ºC. (Note: This is the temperature of the block coil, actual sample temperature is approximately 95-97 ºC).

7.11 Transfer racks of samples to the block digester and place plastic watch glasses over each digestion vessel. Record the time in the Digestion Log Book.

7.12 Let samples heat for 1 hour.

7.13 Remove racks from the block digester and record the time in the Digestion Log Book.

7.14 Bring all samples up to 50 mL with DI water using the graduations on the digestion vessels.

7.15 Record the final volumes in the Digestion Log Book and LIMS.

7.16 Filter ALL samples (including Blank, LCS, and LCSD) using the plunge filters. Be careful when applying pressure to avoid bursting one of the filters. (Reminder: Be sure that the filter side is toward the bottom. Discard handle after use).

7.17 Cap all samples.

7.18 Place samples in batch holders, in the order that they are listed in the Digestion Log Book.

7.19 Calibration, analysis and calculation are not applicable to this SOP but are addressed in the appropriate analytical SOP.

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

9. QA/QC

9.1 Follow the QA/QC protocol outlined in the appropriate analytical SOP.

10. REPORTING

10.1 Not applicable

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

12. REFERENCES

12.1 EPA Methods 3050B and 6010B

Appendix A

Initial Demonstration of Capability (IDC)
Preparation of Solid Samples for ICP/Flame AA

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form ‘IDC 4 rep with RPD’, the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: 80.0-120%
   Precision: $\leq$ 20 % RPD

7. The reagent blank must be less than the reporting limit (RL).

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee’s personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

DOCUMENT REVIEW

DOCUMENT:	LABENV-043.4
REVIEWER:	Cynthia Schultz
DATE:	04/03/08

SECTION	**CHANGES**
Cover Page	Updated to new form

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR TESTING BY ICP OR FLAME AA

SOP NO.: LABENV-042.5

Original Information		
Prepared by:	William R. Dahl	Date: 01/30/02
Technical Review:	Brian Leigh	Date: 02/26/02
QA/QC Coordinator:	Terri Olson	Date: 02/26/02
Authorized by:	Cheryl Sykora	Date: 02/26/02

Revision Information		
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Revised by:	Cynthia Schultz	Date: 04/03/08
Signature:	______________________	Date: __________
Technical Review:	Jaime Zwers	Date: 04/03/08
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 04/07/08
Signature:	______________________	Date: __________

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LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR TESTING BY ICP OR FLAME AA

SOP NO.: LABENV-042.5

Original Information		
Prepared by:	William R. Dahl	Date: 01/30/02
Technical Review:	Brian Leigh	Date: 02/26/02
QA/QC Coordinator:	Terri Olson	Date: 02/26/02
Authorized by:	Cheryl Sykora	Date: 02/26/02

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Revised by:	Cynthia Schultz	Date:
Signature:	______________________	Date: __________
Technical Review:	Jaime Zwers	Date:
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 4/7/08

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FORM GEN-021 (05/07)

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR TESTING BY ICP OR FLAME AA
SOP NO.: LABENV-042.5

Original Information		
Prepared by:	William R. Dahl	Date: 01/30/02
Technical Review:	Brian Leigh	Date: 02/26/02
QA/QC Coordinator:	Terri Olson	Date: 02/26/02
Authorized by:	Cheryl Sykora	Date: 02/26/02

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Supersedes:	LABENV-042.3	Date: 10/08/07
Revised by:	Cynthia Schultz	Date:
Signature:		Date: 4/3/08
Technical Review:	Jaime Zwers	Date:
Signature:		Date: 4/3/08
Authorized by:	Cheryl Sykora	Date:
Signature:		Date:

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SOP TITLE: PREPARATION OF AQUEOUS SAMPLES FOR TESTING BY ICP OR FLAME AA

1. PURPOSE

1.1 This document defines the preparation of samples prior to analysis by ICP or Flame AA. It applies to all aqueous matrices and to terminology referring to "liquids" and "TCLP extracts/leachates." The SOP is applicable to samples typically prepared by EPA Methods 200.7 and EPA 3005A.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the SOP.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This method is appropriate to aqueous liquids with a density around 1 g/mL. If a sample does not fit this criterion it must be prepared using a solid preparation method and reported on a weight basis.

3.2 If the laboratory will be filtering the sample for dissolved metals analyses, do not perform nitric acid preservation.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 Safety glasses and gloves should be worn when handling samples and reagents.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample's integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample's integrity.

5.3 Water samples should be collected in polyethylene or glass containers and preserved with 1:1 nitric acid to a pH < 2.

5.4 The recommended holding time for water samples is six months.

5.5 If a sample is received with pH > 2 then it is preserved in the laboratory and allowed to sit for a minimum of 24 hours at which time the pH is re-tested. If pH < 2, proceed. If not, repeat until pH is < 2, if possible. Highly alkaline samples may need to be digested at reduced volume with excess acid, rather than dilute the original sample in an attempt to lower the pH.

5.6 Document the final pH of all samples in the Digestion Log Book under “Comments.”

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 Block digester

6.2 Screw cap digestion vessels

6.3 Plastic watch glasses

6.4 Nitric acid (HNO_3) 1:1 (trace metal grade :DI)

6.5 Hydrochloric Acid (HCl) 1:1 (trace metal grade :DI)

6.6 Plunge filters

6.7 Deionized (DI) water (>16.3 MΩ)

7. PROCEDURE

7.1 Fill out the appropriate information in the Digestion Log Book, including sample numbers to be prepared. Confirm sample ID and requested analyte information with the Chain-of-Custody (c-o-c).

7.2 For Quality Control (QC), indicate the prep batch # under the sample ID for the Blank, Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD). The LCS is also referred to as the Laboratory Fortified Blank (LFB) or Blank Spike (BS). The prep batch number is obtained from LIMS.

7.3 TCLP samples are batched separately from other aqueous samples.

7.4 Label digestion vessels with sample IDs. Label digestion vessels for the Blank, LCS, and LCSD including the batch number. Along with the sample ID, label MS for sample matrix spike and MSD for sample matrix spike duplicate. MS is also referred to as the Laboratory Fortified Matrix (LFM).

7.5 Shake all samples prior to transferring into digestion vessels.

7.6 Measure out 50 mL of DI water for each of the Blank, LCS, and LCSD using graduations on the digestion vessels. If the batch is TCLP samples, measure out 10 mL of the TCLP leachate blank for each of the Blank, LCS and LCSD and dilute to 50 mL with DI water.

7.7 Measure out 50 mL of each sample into its assigned digestion vessel. Measure directly into digestion vessels using the graduations on the side of the vessels. Graduation marks are certified for volume. Records are kept in the QA/QC department. If the batch is TCLP samples, measure out 10 mL of each TCLP sample into the appropriate digestion vessel and

dilute to 50 mL with DI water.

7.8 For one of the water samples, measure out two additional aliquots, one for the MS and one for the MSD.

7.9 Alternate volumes may be used if sample is limited or a dilution is required.

7.10 Record the initial volumes of all samples in the Digestion Log Book and LIMS.

7.11 Measure out up to 20 samples per batch. If less than 20 samples are measured, “Z” out remaining spaces in the Digestion Log Book, initial, and date.

7.12 Transfer the samples to a rack. Order the samples in the rack from left to right on the long row as they appear in the Digestion Log Book. The labels for the LCS, LCSD, MS and MSD are seen in the first row.

7.13 A typical spike list is given in the table below. Add 0.050 mL for each of the three groups listed below to the LCS, LCSD, MS, and MSD (final volume is 50 mL). For a batch of TCLP samples, spike 0.10 mL of each of the three groups listed below. Final concentrations will be double those listed. Record all information in the Digestion Log Book and LIMS.

Parameter	**Stock Concentration (ppm)**	**Final Concentration (ppm)**
Aluminum	2000	2.0
Barium	400	0.40
Calcium	4000	4.0
Cobalt	400	0.40
Iron	2000	2.0
Magnesium	4000	4.0
Manganese	400	0.40
Potassium	2000	2.0
Sodium	4000	4.0
Vanadium	400	0.40
Zinc	400	0.40

Arsenic	400	0.40
Beryllium	40	0.040
Cadmium	400	0.40
Chromium	400	0.40
Copper	400	0.40
Lead	400	0.40
Nickel	400	0.40
Selenium	400	0.40
Silver	40	0.040
Thallium	400	0.40

Antimony	400	0.40
Boron	400	0.40
Molybdenum	400	0.40
Tin	400	0.40

7.14 Add 4 mL of 1:1 HNO_3 and 5 mL 1:1 HCl to all the samples (including Blank, LCS, & LCSD).

7.15 Ensure the block digester temperature meter reads 120 °C. (Note: This is the temperature of the block coil; actual sample temperature is approximately 95-97 °C).

7.16 Transfer racks of samples to the block digester and place plastic watch glasses over each digestion vessel. Record the time in the Digestion Log Book.

7.17 Let samples heat for 2 to 3 hours, ensuring sufficient volume loss.

7.18 Remove samples from block digester and record the time in the Digestion Log Book. Allow samples to cool.

7.19 Bring all samples up to 50 mL with DI water using the graduations on the digestion vessels.

7.20 Record the final volumes in the Digestion Log Book and LIMS.

7.21 If sediment is present, filter only those samples using the plunge filters. It is imperative that you also filter the QC at this point, including the Blank, LCS, and LCSD. If samples are not being filtered, the QC does not need to be filtered.

7.22 Cap all samples.

7.23 Place samples in batch holders in the order that they are listed in the Digestion Log Book.

7.24 Calibration, analysis and calculation are not applicable to this SOP but are addressed in the appropriate analytical SOP.

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

9. QA/QC

9.1 Follow the QA/QC protocol outlined in the appropriate analytical SOP.

10. REPORTING

Not applicable

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

12. REFERENCES

12.1 EPA Method 200.7

12.2 EPA Methods 3005A and 6010B

Appendix A

Initial Demonstration of Capability (IDC)
Preparation of Aqueous Samples for ICP/Flame AA

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards of all the parameters in lab-grade water and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form ‘IDC 4 rep with RPD’, the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: 200.7 = 85.0-115%, 6010B– 80.0-120% (200.7/6010B may be combined if tighter limits are used for acceptance)
   Precision: 200.7/6010B = $\leq$ 20 % RPD

7. The reagent blank must be less than the reporting limit (RL).

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee’s personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

DOCUMENT REVIEW

DOCUMENT:	LABENV-042.5
REVIEWER:	Cynthia Schultz
DATE:	04/03/08

SECTION	**CHANGES**
	No new updates to SOP

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF NITROAROMATICS, NITRAMINES, AND PETN IN WATER BY HPLC

SOP NO.: LABENV-040.5

Original Information		
Prepared by:	Kimberly Dublin	Date: 08/14/00
Technical Review:		Date:
Technical Director:		Date:
QA/QC Coordinator:	Sharon Dahl	Date: 08/14/00
Authorized by:	Cheryl Sykora	Date: 09/28/00

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Supersedes:	LABENV-040.4	Date: 12/12/05
Revised By:	Scott Creekmur	Date: 02/20/07
Signature:	____________________	Date: __________
Technical Review:	Erica Nastrom	Date: 02/20/07
Signature:	____________________	Date: __________

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SOP TITLE: DETERMINATION OF NITROAROMATICS, NITRAMINES, AND PETN IN WATER BY HPLC

1. PURPOSE

1.1 This document defines the procedure to be followed for the determination of nitroaromatics, nitramines, and PETN in waters by HPLC using a photo diode array (PDA) detector. The SOP is applicable to samples typically analyzed by a modified EPA Method 8330.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the standard operating procedure.

2.3 An analyst trained by LEGEND Technical Services, Inc. shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 The procedure is limited to water samples.

3.2 Degradation products of tetryl appear as a shoulder on the 2,4,6-Trinitrotoluene peak. Peak heights, rather than peak areas, should be used when tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-Trinitrotoluene.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 When working with organic compounds, wear solvent resistant gloves.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample’s integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample’s integrity.

5.3 Water samples should be collected in 1L amber bottles with Teflon lined caps and stored at 4 ± 2 °C. Samples must be protected from light.

5.4 The recommended holding time for water samples is 7 days until extraction, and analysis within 40 days of extraction.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 HPLC with photodiode array detector (PDA)

6.2 Restek Ultra C-18 column 25 cm x 4.6 mm x 5 μm, or equivalent

6.3 Balance – capable of reading 0.1 g

6.4 Vacuum pump

6.5 Solid phase manifold

6.6 3M Empore discs SBD-RPS catalog #2241, or equivalent

6.7 Erlenmeyer flasks

6.8 Buchner funnel

6.9 Filter paper – Whatman #42 or equivalent

6.10 Waste collection container

6.11 Amber serum vials, 10 mL

6.12 Amber autosampler vials

6.13 Acrodisc (0.45 μm) – PTFE, or equivalent

6.14 Graduated cylinder – 500 mL

6.15 25 μL to 1.0 mL analytical syringes

6.16 Disposable syringes – 3 mL, or equivalent

6.17 Graduated disposable pipettes – 1.0 mL and 5 mL, or equivalent

6.18 Reagent water

6.19 Acetonitrile (ACN), HPLC grade

6.20 Methanol (MeOH), HPLC grade

6.21 Calcium chloride ($CaCl_2$), 50 g/L solution – dissolve 5 g of calcium chloride in approximately 70 mL of reagent water, bring to a final volume of 100 mL with reagent water and mix well

6.22 8330 Calibration/Spike Stock – 1,000 ppm EPA 8330 Kit – Restek #31450 and #31451, or equivalent

6.23 Surrogate Stock – 1,000 ppm 1,2-dinitrobenzene, Restek # 31453, or equivalent

6.24 PETN Calibration/Spike Stock – 1,000 ppm PETN, Restek # 31600, or equivalent

6.25 Second Source 8330 Stock – 1,000 ppm, different vendor or different lot number than stock used for calibration

6.26 Second Source PETN Stock – 1,000 ppm, different vendor or different lot number than stock used for calibration

6.27 Second Source Surrogate Stock – 1,000 ppm, different vendor or different lot number than stock used for calibration

6.28 8330/PETN Continuing Calibration (CCAL) Intermediate Solution – dilute 50 µL each of the 1,000 ppm Second Source 8330 Stock, 1,000 ppm Second Source PETN Stock and 1,000 ppm Second Source Surrogate Stock to 10 mL with acetonitrile to produce a 5,000 ng/mL 8330/PETN Continuing Calibration (CCAL) Intermediate Solution

6.29 8330 Spike Working Solution – dilute 1.0 mL each of the 1,000 ppm 8330 Calibration/Spike Stock and the 1,000 ppm PETN Calibration/Spike Stock to 25 mL with acetonitrile to produce a 40 ppm 8330 Spike Working Solution

6.30 Surrogate Working Solution – dilute 1.0 mL of the 1,000 ppm Surrogate Stock to 25 mL with acetonitrile to produce a 40 ppm Surrogate Working Solution

7. PROCEDURE

7.1 Preparation of Samples

7.1.1 Set up filtering apparatus using vacuum pump, Buchner funnel, and Whatman #42 filter paper.

7.1.2 Measure out 500 mL of sample using a graduated cylinder and filter. Repeat with all samples. In each analytical batch choose a sample and measure out two additional aliquots – one for the Matrix Spike (MS) and one for the Matrix Spike Duplicate (MSD).

7.1.3 Measure out 500 mL of reagent water using a graduated cylinder for the method blank and Laboratory Control Spike (LCS).

7.1.4 Add 0.5 mL of the 40 ppm Surrogate Working Solution to each sample filtrate, blank, LCS, and spike sample filtrate.

7.1.5 Add 0.5 mL of the 40 ppm 8330 Spike Working Solution to the filtrate of the samples in each analytical batch selected for spiking. A typical batch will have an LCS and MS/MSD (an LCS/LCSD will be substituted if insufficient sample is provided).

7.1.6 Set up the solid phase manifold with one 3M Empore disc per sample.

7.1.7 Add 40 mL reagent water to the disc and let stand for approximately 5 minutes. Filter through disc until almost dry (5 mL left). DO NOT LET EMPORE DISC GO DRY.

7.1.8 Add 5 mL MeOH to the disc and let stand for approximately 5 minutes. Filter through disc until almost dry. DO NOT LET EMPORE DISC GO DRY.

7.1.9 Pour sample onto Empore disc and filter until dry.

7.1.10 Place a 10 mL amber vial in manifold column under an Empore disc. Add 5 mL ACN and let stand for approximately 5 minutes. Filter ACN into 10 mL vial.

7.1.11 Bring up to 5 mL final volume in ACN using a graduated 5 mL pipette.

7.1.12 Combine 500 µL of the extract and 500 µL of the calcium chloride solution to create a 1:1 solution and mix thoroughly. Filter the 1:1 solution through a 0.45 µm PTFE acrodisc and place the filtrate in an autosampler vial.

7.1.13 The final surrogate and spike concentration is 2000 ng/mL.

7.1.14 Retain the remainder of the extract in a Teflon capped vial.

7.2 Calibration

7.2.1 Prepare working standards at a minimum of five concentration levels, ranging from 500 – 7,500 ng/mL, by diluting the 1,000 ppm 8330 Calibration/Spike Stock and the 1,000 ppm PETN Calibration/Spike Stock with acetonitrile. For each calibration stock solution, combine 500 µL with 500 µL of calcium chloride to create a 1:1 solution, mix thoroughly and filter through a 0.45 µm acrodisc into an autosampler vial. A typical calibration curve would be:

Calibration Stock µL/10 mL	$CaCl_2$ Dil. Conc. ng/mL
10	500
20	1,000
50	2,500
100	5,000
150	7,500

7.2.2 The average response factor should be calculated for each analyte. The percent relative standard deviation (%RSD) should be less than 20% for each analyte. If the RSD for any analyte is greater than 20%, review the results (area counts, response factors, and RSD) for those analytes to ensure that the problem is not associated with just one of the calibration standards.

7.2.3 If the problem appears to be associated with a single standard, reprep and/or reanalyze that standard and calculate the RSD again.

7.2.4 If the %RSD is still greater than 20%, construct calibration curves of area versus concentration using a first order or linear fit. Correlation coefficients should be 0.990 or greater.

7.2.5 Calibration curve calculations are found in the QA Manual.

7.2.6 Reporting limit verification (RLV) is checked with each calibration curve by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or flagging data.

7.2.7 All extracts should be stored in the refrigerator in the dark.

7.3 Analysis

7.3.1 HPLC Conditions

7.3.1.1 Restek Ultra C-18 column

7.3.1.2 HPLC Mobile Phase 44:56 H20:MeOH

7.3.1.3 Oven Temperature 30 °C

7.3.1.4 Wavelength 254 nm for the typical 8330 list and 205 nm for PETN

7.3.1.5 Flow Rate 1.0 mL/min, Isocratic run for 25 minutes

7.3.1.6 Injection volume: 50 µL

7.3.2 Sample peak identification will be confirmed by peak retention time and peak spectrum as compared to standards.

7.3.3 If the response for a peak exceeds the working range of the system or the highest standard, dilute the extract with acetonitrile and re-analyze.

7.3.4 Prepare the CCAL by combining 500 µL of the 8330/PETN Continuing Calibration (CCAL) Intermediate Solution and 500 µL of the calcium chloride solution to create a 1:1 solution and mix thoroughly. Filter the 1:1 solution through a 0.45 µm PTFE acrodisc into an autosampler vial. The final concentrations of the 8330 compounds, PETN, and surrogate are 2,500 ng/mL.

7.3.5 The CCAL is analyzed at the beginning of the run in triplicate (if an initial calibration curve was not analyzed), after every ten samples (singly), and at the end of the run (singly). Recoveries for the triplicates should be ± 15% of the initial curve or corrective action should be taken. Recoveries for the continuing and end CCAL should be ± 15% of the triplicate average.

7.3.6 Corrective action may include reanalyzing the CCAL and/or flagging the data in the daily file.

7.4 Calculation

7.4.1 Computer software calculates the concentration of the sample based on the response. A dilution factor is entered for a 'short cut' to the calculation based on the final volume of the sample. The long form of the calculation yields the final result in ng/mL, which is equal to µg/L.

$$Explosives\ (\mu g / L) = \frac{(F)(CC)(FV)}{V}$$

F = $CaCl_2$ curve factor (0.5 mL std/1.0 mL final volume = 2)
CC = concentration on column (ng/mL)
FV = final volume (mL)
V = volume of sample (mL)

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

8.2 Highly contaminated samples are returned to the client for disposal.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven replicate spikes, when there is a change in the test method that may affect how the test is performed or when there is a major change in instrumentation. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. The method blank must be less than the reporting limit or the sample batch is re-analyzed, if possible. If it is not possible to re-analyze, the data will be flagged where appropriate. Do not subtract analytes in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Accuracy control limits are set at 70.0-130% for LCS, MS and surrogates.

9.3.2 Precision control limits are set at 20.0% RPD (relative percent difference) for LCS/LCSD and MS/MSD.

9.3.3 QC calculations are found in the QA Manual.

9.3.4 LCS, MS and surrogates are reviewed.

9.3.5 If the LCS data are outside the limits, the sample batch is re-extracted and/or re-analyzed, if possible. If the batch cannot be re-extracted and/or re-analyzed, the information is placed in the daily and project files, and a case narrative is written for all client reports within the batch.

9.3.6 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS may be flagged in the case narrative of the report.

9.3.7 If a sample surrogate is outside the limits, the sample is re-extracted and/or reanalyzed, if possible. If the sample cannot be re-extracted and/or reanalyzed, the data is flagged next to the actual result in the report.

10. REPORTING

10.1 Samples results are reported in µg/L.

10.2 The reported result is rounded to two significant figures.

10.3 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A – Initial Demonstration of Capability

11.2 Appendix B – Method Detection Limits and Reporting Limits

12. REFERENCES

12.1 EPA Method 8000B

12.2 EPA Method 8330

Appendix A

Initial Demonstration of Capability (IDC)
Determination of Nitroaromatics and Nitramines

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards in lab-grade water and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

    - Analyst
    - Test/procedure
    - Matrix
    - Date of testing
    - Results

5. Using LEGEND form ‘IDC 4 rep with RPD’, the individual results are entered. The mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

    Accuracy: LCS limits (70.0-130%)
    Precision: LCS limits (≤ 20% RPD)

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the analyst, supervisor, and QA/QC Coordinator sign the form and a copy of the form is placed in the employee’s personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
Nitroaromatics and Nitramines – EPA Method 8330(M)

Parameter	Water MDL (µg/L)	Water RL (µg/L)
1,3,5-Trinitrobenzene	0.29	10
1,3-Dinitrobenzene	0.25	10
2,4,6-Trinitrotoluene	0.87	10
2,4-Dinitrotoluene	0.39	10
2,6-Dinitrotoluene	0.58	10
2-Amino-4,6-dinitrotoluene	0.43	10
2-Nitrotoluene	0.53	10
3-Nitrotoluene	0.34	10
4-Amino-2,6-dinitrotoluene	0.98	10
4-Nitrotoluene	0.32	10
HMX	0.52	10
Nitrobenzene	0.68	10
PETN	1.4	10
RDX	0.45	10
Tetryl	0.56	10

DOCUMENT REVIEW

DOCUMENT:	LABENV-040.5 SOP
REVIEWER:	Scott Creekmur
DATE:	02/20/07

SECTION	**CHANGES**
6.2	Changed ‘Supelcosil LC-8 column’ to ‘Restek Ultra C-18 Column’
6.3	Removed ‘Supelcosil LC-PAH column’, resulted in renumbering of section
6.6	Added ‘SBD-RPS catalog #2241’.
6.8	Added ‘Buchner funnel’
6.15	Added ‘25 µL to 1.0 mL analytical syringes’
6.16	Added ‘Disposable’ and ‘or equivalent’
6.20	Changed ‘Isopropyl Alcohol (IPA), HPLC grade’ to ‘Methanol (MeOH), HPLC grade’
6.22	Changed ‘Supelco’ to ‘Restek’
6.23	Added ‘Restek # 31453, or equivalent’
6.24	Added ‘PETN Calibration/Spike Stock – 1000 ppm PETN, Restek #31600, or equivalent’
6.26	Added ‘Second Source PETN Stock – 1,000 ppm, different vendor or different lot number than stock used for calibration’
6.27	Added ‘Second Source Surrogate Stock – 1,000 ppm, different vendor or different lot number than stock used for calibration
6.28	Added prep of ‘8330/PETN Continuing Calibration (CCAL) Intermediate Solution’
6.29	Revised the 8330 Spike Working Solution prep instructions
6.30	Revised the Surrogate Working Solution prep instructions
7.1.2	Changed ‘For one of the water samples’ to ‘In each analytical batch choose a sample and’
7.1.8	Changed ‘ACN’ to ‘MeOH’
7.1.12	Combined 7.1.13 and 7.1.14 to ‘Combine 500 µL of the extract and 500 µL of the calcium chloride solution to create a 1:1 solution and mix thoroughly. Filter the 1:1 solution through a 0.45 µm PTFE acrodisc and place the filtrate in an autosampler vial.’
7.1.14	Deleted ‘for HPLC analysis’
7.2.1	Revised preparation of working standards

DOCUMENT REVIEW

DOCUMENT:	LABENV-040.5 SOP
REVIEWER:	Scott Creekmur
DATE:	02/20/07

SECTION	**CHANGES**
7.2.2	Deleted calibration calculations
7.2.5	Added 'Calibration curve calculations are found in the QA Manual'
7.2.6	Added RLV statement
7.3.1	Revised HPLC conditions
7.3.2	Deleted confirmation HPLC conditions and added 'Sample peak identification will be confirmed by peak retention time and peak spectrum as compared to standards'
7.3.4	Added prep of CCAL
7.3.7	Deleted 'Any positive detection above the RL is compared with a spectral library for confirmation'
9.3.3	Added 'QC calculations are found in the QA Manual'
Appendix B	Updated MDLs; separated 2-nitrotoluene and 4-nitrotoluene; added PETN
Cover Page	Updated to new form
SOP Form	Updated to new form with current address
Title	Added PETN to SOP title

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: ANALYSIS OF SAMPLES BY AXIAL ICP-AES

SOP NO.: LABENV-039.5

Original Information		
Prepared by:	William Dahl	Date: 05/24/00
Technical Review:	Sharon Dahl	Date: 05/24/00
QA/QC Coordinator:		Date:
Authorized by:	Cheryl Sykora	Date: 09/28/00

Revision Information		
Supersedes:	LABENV-039.4	Date: 04/27/07
Revised by:	Cynthia Schultz	Date: 04/03/08
Signature:	______________________	Date: __________
Technical Review:	Jaime Zwers	Date: 04/03/08
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date: 04/07/08
Signature:	______________________	Date: __________

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LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: ANALYSIS OF SAMPLES BY AXIAL ICP-AES

SOP NO.: LABENV-039.5

Original Information		
Prepared by:	William Dahl	Date: 05/24/00
Technical Review:	Sharon Dahl	Date: 05/24/00
QA/QC Coordinator:		Date:
Authorized by:	Cheryl Sykora	Date: 09/28/00

Revision Information		
Supersedes:	LABENV-039.4	Date: 04/27/07
Revised by:	Cynthia Schultz	Date:
Signature:	______________________	Date: __________
Technical Review:	Jaime Zwers	Date:
Signature:	______________________	Date: __________
Authorized by:	Cheryl Sykora	Date:
Signature:	Cheryl Sykora	Date: 4/7/08

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FORM GEN-021 (05/07)

LEGEND TECHNICAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

TITLE: ANALYSIS OF SAMPLES BY AXIAL ICP-AES

SOP NO.: LABENV-039.5

Original Information		
Prepared by:	William Dahl	Date: 05/24/00
Technical Review:	Sharon Dahl	Date: 05/24/00
QA/QC Coordinator:		Date:
Authorized by:	Cheryl Sykora	Date: 09/28/00

Revision Information		
Supersedes:	LABENV-039.4	Date: 04/27/07
Revised by:	Cynthia Schultz	Date:
Signature:	[signature]	Date: 4/3/08
Technical Review:	Jaime Zwers	Date:
Signature:	[signature]	Date: 4/3/08
Authorized by:	Cheryl Sykora	Date:
Signature:		Date:

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SOP TITLE: ANALYSIS OF SAMPLES BY AXIAL ICP-AES

1. PURPOSE

1.1 This document defines the analysis for various metals by axially viewed inductively coupled plasma atomic emission spectroscopy (ICP-AES). The SOP is applicable to samples typically analyzed by EPA 200.7, EPA 6010B, and a modified NIOSH 7303.

2. RESPONSIBILITY/PERSONNEL

2.1 It is the responsibility of the designated quality assurance supervisor to ensure this procedure is followed.

2.2 It is the responsibility of the laboratory analyst to perform all quality control steps as defined in the SOP.

2.3 An analyst trained by Legend Technical Services, Inc. (LEGEND) shall perform the analysis. Each new analyst performs an Initial Demonstration of Capability (IDC). The IDC information can be found in Appendix A.

3. PROCEDURE LIMITATIONS

3.1 This method is applicable to digestates of various matrices.

4. HEALTH AND SAFETY

4.1 Read all Material Safety Data Sheets (MSDS) associated with the chemicals used in this procedure.

4.2 Follow standard laboratory safety practices.

4.3 Safety glasses and gloves should be worn when handling samples and reagents.

5. SAMPLE COLLECTION/ACCEPTANCE/REJECTION

5.1 The sample shall be accepted if packaged to protect the sample’s integrity and clearly labeled for identification.

5.2 The sample shall not be accepted if it is not clearly identified or packaged so as to protect the sample’s integrity.

5.3 Water samples should be collected in polyethylene or glass containers and preserved with 1:1 nitric acid to a pH < 2. Samples to be filtered in the laboratory should be collected in an unpreserved bottle.

5.4 If a water sample is received with pH > 2 then it is preserved in the laboratory and allowed to sit for a minimum of 24 hours at which time the pH is re-tested. If pH < 2, proceed. If not, repeat until pH is < 2, if possible. Highly alkaline samples may need to be digested at reduced volume with excess acid, rather than dilute the original sample in an attempt to lower the pH.

5.5 Document pH and/or lab filtration in Digestion Logbook under “Comments”.

5.6 The recommended holding time for water samples is six months.

5.7 Solid samples should be collected in polyethylene or glass containers and stored at 4 ± 2 °C.

5.8 The recommended holding time for solid samples is six months.

6. EQUIPMENT/MATERIALS/REAGENTS

6.1 Varian Model VISTA AX™ ICP-AES Instrument, or equivalent

6.2 Varian Model SPS-5™ Autosampler, or equivalent

6.3 Assorted laboratory glassware

6.4 15 mL disposable centrifuge tubes

6.5 Nitric acid (HNO_3) - concentrated, trace metal grade

6.6 Hydrochloric acid (HCl) - concentrated, trace metal grade

6.7 De-ionized (DI) water (>16.3 MΩ)

6.8 Appropriate purchased traceable single element stock standards

6.9 Calibration Stock Standards - various concentration levels, Inorganic Ventures #LTS-STOCK-1A, #LTS-STOCK-2A, and #LTS-STOCK-3A, or equivalent

6.10 Second Source Stock Standards - various concentration levels, SCP Science #600-218-304, #600-218-305, and #600-218-306

6.11 Interference standards – ICSA (Fe = 300 mg/L and Al, Ca, Mg = 200 mg/L each)

6.12 Liquid Argon Dewars

7. PROCEDURE

7.1 Preparation of Samples

7.1.1 Aqueous samples are prepped for analysis by using the SOP entitled ‘Preparation of Aqueous Samples for Testing by ICP or Flame AA’.

7.1.2 Soil/solid samples are prepped for analysis by using the SOP entitled ‘Preparation of Solid Samples for Testing by ICP or Flame AA’.

7.2 Calibration

7.2.1 Refer to Equipment SOP entitled ‘Inductively Coupled Plasma – Atomic Emission Spectrometer’ for instrument set-up.

7.2.2 The calibration consists of one calibration standard prepared in 4% HNO_3 and 5% HCl from the Calibration Stock Standards and a calibration blank. An example of the calibration level would be:

Element	Level (ppm)	Element	Level (ppm)	Element	Level (ppm)
Ag	0.40	Cr	4.0	Pb	4.0
Al	20	Cu	4.0	S	8.0
As	4.0	Fe	20	Sb	4.0
B	4.0	K	20	Se	4.0
Ba	4.0	Li	4.0	Si	3.7
Be	0.40	Mg	40	Sn	4.0
Ca	40	Mn	4.0	Ti	4.0
Cd	4.0	Na	40	Tl	4.0
Ce	2.0	Ni	4.0	V	4.0
Co	4.0	P	4.0	Zn	4.0

7.2.3 Calibration curve calculations are found in the QA Manual.

7.2.4 Reporting limit verification (RLV) is checked with each calibration curve or monthly at a minimum, by either reprocessing the corresponding calibration level or analyzing a separate standard at or below the reporting limit level. If samples are analyzed less frequently than monthly, the RLV will be checked with the next analysis. The RLV must be ± 40% or corrective action should be taken. Corrective action may include reanalysis, preparing a new standard, performing maintenance, and/or raising the reporting limit. The RLV (CRDL) for AIHA (ELLAP) samples must be ± 20%.

7.3 Analysis

7.3.1 Standards required for each method's analysis are outlined below.

7.3.2 Method EPA 6010B and AIHA (ELLAP)

7.3.2.1 Continuing Calibration Verification (CCV). This is a multi-element, mid-level standard in 4% HNO_3 and 5% HCl prepared from the Calibration Stock Standards. It is analyzed following the calibration, after every 10 samples, and at the end of the run. Elements of interest must recover within ± 10% of the true value. If not, samples bracketed by an out-of-spec CCV must be re-analyzed.

7.3.2.2 Continuing Calibration Blank (CCB). This is the Calibration Blank, a 4% HNO_3/5% HCl solution in DI water. It is analyzed following the calibration, after every 10 samples, and at the end of the run. For elements of interest, the absolute value of the result must be less than the reporting limit. If not, samples bracketed by an out-of-spec CCB must be re-analyzed.

7.3.2.3 Initial Calibration Verification (ICV). This is a multi-element standard in 4% HNO_3 and 5% HCl prepared from the Second Source Stock Standards. It is analyzed following the calibration and must recover within ± 10% of the true value. If this fails, no data can be reported for analytical lines out of control.

7.3.2.4 Interference Check Standard A (ICSA). This is a multi-element standard in 4% HNO_3 and 5% HCl prepared from the Fe, Al, Ca, and Mg single element stock standards. The ICSA is used to verify the inter-element corrections (IEC) of the analytical method and consists of Fe at 300 mg/L, and Al, Ca, and Mg at 200 mg/L. It is analyzed after the calibration and before samples. The absolute value of the analytes of interest (other than Fe, Al, Ca & Mg) must be less than the value of the reporting limit. The ICSA is also analyzed at the end of the run.

7.3.2.5 Iron (Fe) and Aluminum (Al) Spectral Interference Check (SIC) Solutions. These are single element standards (Fe at 300 mg/L and Al at 200 mg/L) in 4% HNO_3 and 5% HCl prepared from the Fe and Al single element stock standards. The Fe and Al SIC Solutions are used to verify and/or correct for interferences from Fe and Al. They are analyzed with every run, as Fe and Al are the most prevalent source of interferences on environmental samples. If an interference is present, IEC factors are re-calculated based on the response from these standards and the run re-processed to reflect these corrections.

7.3.2.6 Spectral Interference Check (SIC). These are single element standards analyzed annually to validate IEC factors for all corrections (not just Fe, Al, Ca, Mg). These are elements known to have potential spectral overlaps with analytes of interest. The following elements are measured: Fe, Al, Ba, Be, Cd, Ce, Co, Cr, Cu, Mn, Ni, Si, Sn, Ti, Tl, V, Zn, Pb, and Mo. If an interference is detected, IEC factors are re-calculated and the method is updated.

7.3.2.7 Linear Dynamic Range (LDR) Determination. The linear dynamic range must be determined annually or when a new method is developed. Standards are measured at successive levels with the criteria being that the standards recover within ± 10% of the true value. Samples outside the LDR are diluted and re-analyzed.

7.3.3 Method EPA 200.7

7.3.3.1 Instrument Performance Check (IPC): This is identical to the CCV above. This is a multi-element, mid-level standard in 4% HNO_3 and 5% HCl prepared from the Calibration Stock Standards. It is analyzed following the calibration, after every 10 samples, and at the end of the run. The first IPC (CCV) must recover within ± 5% of the true value. If this fails for any of the elements of interest, the run must be stopped and the instrument recalibrated. Continuing IPC (CCV) determinations must recover within ±10% of true value. If this fails for any of the elements of interest, samples bracketed by an out-of spec IPC (CCV) must be re-analyzed following recalibration of the instrument.

7.3.3.2 Calibration Blank Check. This is identical to the CCB above. This is the Calibration Blank, a 4% HNO_3/5% HCl solution in DI water. It is analyzed following the calibration, after every 10 samples, and at the end of the run. For elements of interest, the absolute value of the result must be less than the reporting limit. If not, samples bracketed by an out-of-spec Calibration Blank must be re-analyzed.

7.3.3.3 Quality Control Sample (QCS). This is identical to the ICV above. This is a multi-element standard in 4% HNO_3 and 5% HCl prepared from the Second Source Stock Standards. It is analyzed following the calibration and must recover within ± 5% of the true value. If this fails for any of the elements of interest, the run must be stopped and the instrument re-calibrated.

7.3.3.4 Interference Check Standard A (ICSA). This is a multi-element standard in 4% HNO_3 and 5% HCl prepared from the Fe, Al, Ca, and Mg single element stock standards. The ICSA is used to verify the inter-element corrections (IEC) of the analytical method and consists of Fe at 300 mg/L, and Al, Ca, and Mg at 200 mg/L. It is analyzed after the calibration and before samples. The absolute value of the analytes of interest (other than Fe, Al, Ca & Mg) must be less than the value of the reporting limit. The ICSA is also analyzed at the end of the run.

7.3.3.5 Iron (Fe) and Aluminum (Al) Spectral Interference Check (SIC) Solutions. These are single element standards (Fe at 300 mg/L and Al at 200 mg/L) in 4% HNO_3 and 5% HCl prepared from the Fe and Al single element stock standards. The Fe and Al SIC Solutions are used to verify and/or correct for interferences from Fe and Al. They are analyzed with every run, as Fe and Al are the most prevalent source of interferences on environmental samples. If an interference is present, IEC factors are re-calculated based on the response from these standards and the run re-processed to reflect these corrections.

7.3.3.6 Spectral Interference Check (SIC). These are single element standards analyzed annually to validate IEC factors for all corrections (not just Fe, Al, Ca, Mg). These are elements known to have potential spectral overlaps with analytes of interest. The following elements are measured: Fe, Al, Ba, Be, Cd, Ce, Co, Cr, Cu, Mn, Ni, Si, Sn, Ti, Tl, V, Zn, Pb, and Mo. If an interference is detected, IEC factors are re-calculated and the method is updated.

7.3.3.7 Linear Dynamic Range (LDR) Determination. The linear dynamic range must be determined annually or when a new method is developed. Standards are measured at successive levels with the criteria being that the standards recover within ± 10% of the true value. Samples are valid up to 90% of the determined LDR. For example, a 100 mg/L standard is analyzed and reads 95 mg/L. This would validate the LDR to 100 mg/L; however, samples can only be validated to 90 mg/L (90% of the LDR). Samples outside the LDR are diluted and re-analyzed.

7.3.4 Validate IEC corrections for Iron and Aluminum at the end of each instrument run. Reprocess run as necessary.

7.3.5 Samples with an in-solution concentration greater than the calibration level for an analyte of interest must be diluted such that the result falls below the calibration concentration if possible. If not, data must be flagged and qualified.

7.3.6 Export 'in solution' data for the run into LIMS.

7.4 Calculation

7.4.1 The concentration of the analyte in the sample is calculated using the following equations:

$$Water\ Concentration\ (mg/L) = \frac{(C_{in})(FV)(D)}{V}$$

$$Soil\ Concentration\ (mg/kg) = \frac{(C_{in})(FV)(D)}{M}$$

C_{in} = in-solution concentration, µg/mL
FV = final volume, mL
D = dilution factor
V = volume of sample, mL
M = mass of sample, g

7.5 Print a copy of the data from the LIMS for each project for internal validation.

7.6 Sign and date the data sheets and the raw data checklist found in the run.

7.7 Submit data sheets and raw data to a qualified Chemist for peer review. Peer reviewer signs and dates the data sheets and the raw data checklist after checking data for integrity as well as compliance to protocols.

7.8 Turn data sheet into the Client Manager.

7.9 Archive paper copy of raw data in Inorganic Daily Files.

7.10 Electronic copies of the raw data are stored on the network.

8. WASTE DISPOSAL

8.1 Dispose of all samples and analysis materials in accordance with current company waste disposal procedures.

8.2 Retain samples for two months after the prep date.

8.3 Samples and digestates are disposed of in the acid neutralizing laboratory sinks.

9. QA/QC

9.1 MDL, PQL, RL

9.1.1 Method detection limits (MDLs) and practical quantitation limits (PQLs) are updated, using at least seven digested replicate spikes, on an annual basis. Reporting limits (RLs) are based on a combination of MDL/PQL studies, interference studies, client requirements, and analyst experience. Data are not always reproducible at statistical MDL and PQL levels; therefore, judgment is used to determine actual RL. The RL used must be greater than or equal to the calculated PQL. Current MDLs and RLs values can be found in Appendix B. Project specific RLs may override those listed.

9.2 Method Blank

9.2.1 A method blank is analyzed with each batch of up to 20 samples prepared at the same time. The method blank must be less than the reporting limit or the sample batch is redigested if possible. If it is not possible to redigest, the data will be flagged where appropriate. Do not subtract compounds in the blank from sample results. Report all blank results with the samples.

9.3 Control Limits

9.3.1 Accuracy control limits are set at the following:

9.3.1.1 EPA 200.7 LCS = 85.0-115%.

9.3.1.2 EPA 6010B LCS and NIOSH 7303(M) = 80.0-120%.

9.3.1.3 EPA 200.7 and 6010B MS = 75.0-125%.

9.3.2 Precision control limits are set at $\leq$ 20% RPD.

9.3.3 QC calculations are found in the QA Manual

9.3.4 LCS and MS are reviewed.

9.3.5 If the LCS data are outside the limits, a method nonconformance is filled out and the sample batch is re-digested if possible. If the batch cannot be re-digested, the data are flagged and/or a case narrative is written for all client reports within the batch.

9.3.6 If the MS data are outside the limits (the LCS has all ready been reviewed and is acceptable), the information is placed in the daily and project files, and the data for that specific MS is flagged and/or a case narrative is written.

10. REPORTING

10.1 Solid sample results are reported in mg/kg on a dry weight basis.

10.2 Bulk sample results are reported in mg/kg on an as received basis.

10.3 Water sample results are reported in mg/L.

10.4 The reported result is rounded to two significant figures.

10.5 The results are placed in the client file and a final report is sent to the client.

11. APPENDICES

11.1 Appendix A - Initial Demonstration of Capability

11.2 Appendix B - Method Detection Limits and Report Limits

12. REFERENCES

12.1 EPA 200.7 rev 4.4 (May 1994)

12.2 EPA 6010B

12.3 Varian Model Vista AX™ ICP Atomic Emission Spectrometer Operating Manual

Appendix A

Initial Demonstration of Capability (IDC)
Axial ICP-AES

1. Prior to using any existing published method, and at any time there is a significant change in the published test method, instrument type or personnel, a demonstration of capability must be made.

2. Prepare four mid-level replicate standards of all the parameters and a reagent blank.

3. Analyze the replicates and reagent blank per the SOP.

4. Compile the following information and give to the QA Department.

   - Analyst
   - Test/procedure
   - Matrix
   - Date of testing
   - Results

5. Using LEGEND form 'IDC 4 rep with RPD', the individual recoveries in concentration and %, the mean recovery in concentration and %, and the % RPD of the replicates are calculated.

6. The results must meet the following criteria:

   Accuracy: EPA 200.7 = 85.0-115%, EPA 6010B = 80.0-120%
   Precision: $\leq$ 20% RPD

7. The reagent blank must be less than the reporting limit (RL) – see Appendix B.

8. If the IDC is acceptable, the QA/QC Coordinator signs the form and a copy of the form is placed in the employee's personnel folder.

9. If the IDC is not acceptable, it will be reanalyzed.

Appendix B

Method Detection Limits and Reporting Limits
Axial ICP-AES

Parameter	Water MDL (mg/L)	Water RL (mg/L)	Soil MDL (mg/kg)	Soil RL (mg/kg)
Aluminum	0.00017	0.020	0.0085	1.0
Antimony	0.0011	0.010	0.0055	0.50
Arsenic	0.0020	0.010	0.10	0.50
Barium	0.0026	0.020	0.13	1.0
Beryllium	0.00021	0.0050	0.011	0.25
Boron	0.0063	0.10	0.32	5.0
Cadmium	0.000099	0.0010	0.025	0.25
Calcium	0.0077	1.0	0.39	50
Chromium	0.00024	0.010	0.012	0.50
Cobalt	0.00024	0.0050	0.012	0.25
Copper	0.0014	0.020	0.070	1.0
Iron	0.0047	0.050	0.24	2.5
Lead	0.00068	0.0030	0.034	1.0
Magnesium	0.045	1.0	2.3	50
Manganese	0.00048	0.020	0.024	1.0
Molybdenum	0.0023	0.050	0.12	2.5
Nickel	0.00028	0.0050	0.014	0.25
Phosphorous	0.0023	0.050	0.12	2.5
Potassium	0.028	1.0	1.4	50
Selenium	0.0022	0.020	0.11	1.0
Silver	0.00018	0.0050	0.0090	0.25
Sodium (589)	0.020	1.0	1.0	50
Thallium	0.0026	0.040	0.13	2.0
Tin	0.00084	0.020	0.042	1.0
Titanium	0.0010	0.020	0.050	1.0
Vanadium	0.00017	0.0050	0.0085	0.25
Zinc	0.0044	0.020	0.22	1.0

DOCUMENT REVIEW

DOCUMENT:	LABENV-039.5 SOP
REVIEWER:	Cynthia Schultz
DATE:	03/12/08

SECTION	**CHANGES**
Cover Page	Updated to new form
6.12	Added line for ‘Liquid Argon Dewars’
Appendix B	Updated MDLs

DESCRIPTION:

Sample Preparation for MDA list 2 Herbicides in Aqueous Sample Matrices.

SUMMARY:

This procedure is used to prepare aqueous samples for the analysis of MDA list 2 Acid Herbicides. This procedure is based on EPA Method SW-846 8151A and EPA Method SW-846 3510C. Because the List 2 herbicides are produced and used in various forms (i.e. acid, salt, ester, etc.), this method describes a hydrolysis step that can be used to convert herbicide esters into the acid form. The acids are then converted to their methyl esters using diazomethane as the derivatizing agent. The extract is concentrated to a 1mL final volume for analysis.

SCOPE:

This procedure complies with the requirements of the Resource Conservation and Recovery Act (RCRA). This SOP is applicable to the analysis of aqueous samples. This applies to the preparation portion only.

DOCUMENT CONTINUITY:

This SOP replaces MDA2H20PREP revision 2.

SIGNATURES:

Quality Assurance [signature] **Date** 4/16/09
Michelle M. Hubanks

Technical Lead [signature] **Date** 04/09/2009
Rupali Sawant

Laboratory Manager [signature] **Date** 04/14/09
Thomas P. Wagner

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1.0 PERSONNEL QUALIFICATIONS:

1.1 Personnel performing this procedure must be qualified per the requirements outlined in chapter 1 of the Analytical Laboratory Quality Assurance Manual (QAM).

2.0 SAFETY:

2.1 Personnel performing this procedure must follow general laboratory safety practices as defined in chapter 1 of the (QAM).

2.2 When working with organic compounds, wear solvent resistant gloves.

2.3 Diazomethane esterification can be hazardous. The diazomethane reagent is a carcinogen and a mutagen. Diazomethane can explode if exposed to heat or moisture. **Note:** when performing diazomethane esterification, be careful not to breathe the vapors. Perform in a hood and do not allow any contact with the skin.

2.4 A protective face shield should be worn during the diazomethane reagent generation.

3.0 DEFINITIONS:

3.1 Refer to standardized Braun Intertec Corporation definitions as described in chapter 4 of the QAM.

3.2 Leech Lodge: A small Styrofoam cooler that contains steel pellets used in the preparation of the diazomethane reagent.

3.3 KOH: Potassium hydroxide.

3.4 UPDI: Ultra Pure Deionized Water

3.5 H_2SO_4: Sulfuric Acid.

3.6 NaOH: Sodium Hydroxide.

3.7 NaCl: Sodium Chloride.

3.8 QA/QC: Refers to the Quality Group (Quality Director and QA Officer).

3.9 $MeCl_2$: Methylene Chloride.

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3.10 LIMS: Laboratory Information Management System.

3.11 Element: the LIMS used by the Analytical Laboratory.

4.0 FORMS & RECORDS:

4.1 LIMS Bench Sheet, Refer to Appendix A.

4.2 LIMS Standard Record, Refer to Appendix B.

5.0 EQUIPMENT & SUPPLIES:

5.1 Separatory funnel: 2000 mL, Teflon.

5.2 Separatory funnel shaker – Braun design with 8 funnel capacity.

5.3 Erlenmeyer flask: 500 mL.

5.4 TurboVap II concentration work Station.

5.5 200 mL Zymark Turbovap II Concentrator tubes with a 1 mL reservoir.

5.6 Glass stir rods (used for breaking emulsions).

5.7 Diazomethane Generator Kit, Aldrich Chemical Cat # 210,025-0 or equivalent.

5.8 500 mL and 1000 mL Pyrex beakers.

5.9 Hot Plate with stirring mechanism.

5.10 HCl Rinsed Glass wool.

5.11 Thermometer, 1 degree gradients.

5.12 Disposable pipettes – 1 mL, 5 mL and 10 mL.

6.0 REAGENTS & STANDARDS:

6.1 UPDI water: Ultra pure deionized water equivalent to ASTM type1.

6.2 Methylene Chloride: Pesticide grade or equivalent.

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6.3 Methanol: Pesticide grade or equivalent.

6.4 Acetone, pesticide grade.

6.5 Potassium hydroxide, ACS grade.

6.6 Ethanol, pesticide grade.

6.7 Ethyl ether, pesticide grade.

6.8 Diazald, Aldrich Chemical, 99+%.

6.9 Liquid N_2.

6.10 Sulfuric acid (12N) H_2SO_4. Slowly add 335 mL H_2SO_4 to 665 mL of UPDI water. This reagent will get very hot while being made and should be prepared in an Erlenmeyer flask placed in a cold water bath to minimize the hazard. Start by adding the acid to 500 mL of UPDI and bring up to a final volume of 1000 mL.

6.11 Sodium Hydroxide (6N) NaOH. This reagent will get very hot while being made and should be prepared in a cold water bath to minimize the hazard. Add 240 grams of NaOH to 800 mL UPDI water in a one liter volumetric flask. Bring to one liter final volume after adding all NaOH pellets.

6.12 Sodium chloride, ACS grade or equivalent.

6.13 Acidified Sodium Sulfate: (ACS) granular. Prepare a slurry using 1000 g sodium sulfate with enough ethyl ether to just cover the solid, then add 1 mL of concentrated sulfuric acid. Remove the ether under a vacuum or boil away on the steam bath. Mix 1 g of the resulting solid with 5 mL of UPDI water and measure the pH of the mixture. It must be below pH 4. Store in a sealed, dry container.

6.14 Diazomethane reagent – Prepared using the Diazomethane Generation Kit as described 6.14.1-6.14.4. All quantities of reagents may be doubled in order to generate a "double batch" of diazald solution. Note: Extreme care must be taken when performing this step as increasing the batch size increases the potential strength of explosion.

6.14.1 In the reaction vessel, add 10 mL of ethanol to a solution of 5 grams KOH in 8 mL of UPDI water. Attach a 100 mL receiving flask to the condenser and cool the receiver in a leech lodge (small Styrofoam cooler that contains steel pellets) that has been filled to the top of pellets with liquid N_2.

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Attach an ether trap containing approximately 2 mL of ethyl ether to the side arm.

6.14.2 Place the separatory funnel that comes with the Diazomethane Generation Kit over the reaction vessel and fill the funnel with a solution made up of 5 grams diazald in 45 mL ethyl ether. Shake gently or swirl to dissolve the diazald.

6.14.3 Warm the reaction vessel to 65°F and open the separatory funnel so that the rate of distillation is equal to the rate of addition. This rate should be a slow drip.

6.14.4 This reagent is good for approximately 14 days. Discard appropriately after this time.

6.15 Surrogate Solution – 100µg/mL of D.C.A.A.: Prepare by diluting the appropriate amount of stock solution to a 10mL final volume of acetone to achieve 100µg/mL D.C.A.A. Record standard preparation in the LIMS.

6.16 Spike Solution - 100µg/mL of List 2 analytes: Prepare by diluting the appropriate amount of stock solution(s) to a 10mL final volume of acetone to achieve 100µg/mL for each compound. Record standard preparation in the LIMS.

6.17 1 N HCl: In a 1000mL volumetric flask, add 83mL HCl to 900ml UPDI. Bring up to 1000ml final volume with UPDI. Invert several times to mix.

7.0 INTERFERENCES & PROCEDURAL LIMITATIONS:

7.1 Rinse all glassware with methylene chloride before use to ensure glassware is clean and free from contaminants.

7.2 Herbicides are acids and will react with alkaline substances, causing a loss during analysis. To avoid this problem glassware and glass wool should be acid rinsed with 1N HCl. After the acid rinse, rinse the glassware 3 times with each UPDI water, acetone, and methylene chloride (any residual water on TurboVap tubes must be removed completely using acetone and methylene chloride as necessary). Sodium sulfate must also be acidified for this reason.

7.3 To avoid low recoveries, sample extracts must be dry prior to methylation.

8.0 SAMPLE ACCEPTANCE & HOLDING TIMES:

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8.1 Samples must be stored at 4°C from the time of collection to the time of extraction.

8.2 Samples must be extracted within 7 days of sample collection and analyzed within 40 days of extraction.

9.0 CALIBRATION & STANDARDIZATION:

9.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for the calibration and standardization of the GC/MS.

10.0 PROCEDURE:

10.1 Record standard preparation in Element if new standards are needed.

10.1.1 Under Laboratory, click on Standards. Click Add.

10.1.2 For parent standards choose 1. "Specify each analyte and its concentration". Fill in the description, department, expiration date, initials and prepared date. Lot number and additional standard information can be typed in the comment section.

10.1.3 Choose the analytes from the analyte list. To narrow the list, select 8270 MDA List 2 Waters. Select the appropriate compounds from the list and add them to the standard.

10.1.4 Adjust the concentration and the concentration units as necessary.

10.1.5 Make sure the standard type is appropriate (i.e. for spike, click spike. For surrogate, click surrogate).

10.1.6 To prepare child standards click Add and choose 2. "Combine and/ or dilute existing standards."

10.1.7 Fill in the header information and choose the appropriate parent standard(s). Entering the standard volumes and the final volume will adjust the concentration of the child standard. It will not appear until the standard is saved.

10.1.8 Again, make sure the standard type is appropriate.

10.1.9 For standards that are created new but exactly the same as previous standards instead of choosing add, choose copy. The standard can be

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copied so that the analytes and concentrations do not need to be added. Fill in the header information with the correct preparation date and expiration date.

10.2 Create a new batch/bench sheet in Element.

10.2.1 Under Laboratory, click Batch. Click Add to create a new batch.

10.2.2 Choose the preparation method (EPA 3510C), matrix and surrogate. Make sure the surrogate type is pre-prep. In the reagent box, right click and choose the appropriate solvents and reagents used for traceability.

10.2.3 Choose the appropriate analysis and click bench sheet.

10.2.4 On the bench sheet click edit and then add. Choose client samples (by container). Choose all of the samples that will be prepared in that batch. There cannot be more than 20 samples in each batch.

10.2.5 With each batch a MB, BS1, BSD1, MS1, MSD1 will be added. If there is insufficient sample for a MS/MSD pair, a sample duplicate and MS from another sample can be substituted. To remove QC or samples click on the appropriate sample and choose remove. To add QC click add and choose the appropriate QC sample.

10.2.6 To add information such as initial and final volumes, prepared date, prepared by and comments, highlight samples or QC, right click and choose the appropriate command. Be sure to adjust the sample volume to document the actual sample volume used in extraction.

10.2.7 The LCS/LCSD/MS/MSD standard ID can be added by right clicking on each QC sample and choosing the appropriate command. Also fill in the standards type (pre-prep) and the amount spiked. For sample duplicates and MS/MSD the sample source must also be added.

10.2.8 Print the bench sheet using the bch_std06.00.rpt.

10.3 Prepare samples for extraction.

10.3.1 Check the pH of each sample and record on the extraction data sheet.

10.3.2 Mark the water meniscus on the side of the sample bottle for later determination of the sample volume. The sample volume must be documented on the bench sheet and in LIMS on the bench sheet screen. If

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the sample is silty or has suspended solids, decant as much of the waterinto the funnel as possible, without letting the solids into the funnel.

10.3.3 For laboratory control samples (LCS/LCSD/MB) use 1 L of UPDI water as the control matrix.

10.3.4 Deliver 50 µL MDA list 2 surrogate to all samples, including quality control samples.

10.3.5 Deliver 50 µL MDA list 2 spike to the LCS/LCSD and MS/MSD.

10.3.6 Add 250 grams of sodium chloride (NaCl) to each separatory funnel. Seal and shake each funnel to dissolve the salt. The salt may be added half at a time to make the shaking easier. The full 250 grams must be used in order to avoid low recoveries of select List 2 analytes.

10.4 Basic portion of Extraction.

10.4.1 Adjust the pH of all samples and QC to greater than or equal to 12. To do this, add 5 mL of 6N NaOH solution, seal and shake. Confirm the pH using pH test strips for each sample before proceeding. Make a notation on the sample extraction form that the pH was adjusted. Some samples may have a greater buffering capacity requiring additional NaOH. If the pH is less than 12, add more 6N NaOH until a pH of greater than or equal to 12 is reached. Record any extra volume needed on the bench sheet.

10.4.2 Place separatory funnels on shaker and shake for 10 minutes.

10.4.3 Allow samples to stand for 1-2 hours at room temperature for hydrolysis to occur. Shake the separatory funnels by hand periodically during that timeframe.

10.4.4 Add 60 mL methylene chloride to each separatory funnel. Shake each funnel for 2 minutes, venting periodically, then allow the organic portion to separate from the water. The organic portion can then be collected and discarded in the appropriate waste container. Care must be taken to break up emulsions, but the emulsion phase should remain in the separatory funnel. In this initial step, it is important that none of the aqueous phase or emulsion is discarded. If necessary, the analyst should leave a small amount of methylene chloride in the separatory funnel from the clean up step. If the sample is very dirty or if there is a large emulsion, then a second or third shake with additional MeCl2 may be employed for extra cleanup. Discard the additional $MeCl_2$ in an appropriate waste container.

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10.5 Acidic portion of Extraction.

10.5.1 Adjust the pH to less than 2 by adding approximately 5mL of 12 N H_2SO_4. Check the pH and document the pH change on the extraction sheet. Add more 12 N H_2SO_4 if necessary. Record any extra volume needed on the bench sheet. Proceeding with the extraction with a pH of greater than 2 will significantly reduce recoveries.

10.5.2 Add 60 mL methylene chloride to each separatory funnel. Extract the sample by shaking the funnel for 2 minutes, with periodic venting to release pressure.

10.5.3 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between the 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, but may include stirring, filtration of the emulsion through acidified glass wool, sonication or centrifugation. Collect the extract in a prepped (7.2), 500 mL Erlenmeyer flask.

10.5.4 Extract the sample two more times using 60 mL of methylene chloride each time. Combine the extracts in the Erlenmeyer flask. Discard the water in the separatory funnel.

10.6 Dry sample extracts: Add acidified sodium sulfate to each Erlenmeyer flask to dry the extract. Samples should be allowed to stand for at least a 2 hour minimum with periodic swirling, overnight being preferred. If the sodium sulfate clumps, or forms a solid, more must be added until it remains free flowing. Removal of the water from the extract is a critical step, as any remaining water will interfere with the derivatization process. An acidified sodium sulfate powder funnel may also be useful in removal of water when transferring the extract to the Turbovap tube for concentration. If the powder funnel step is performed, all materials must first be pre-rinsed with 1 N HCl, then UPDI water, then acetone to remove water and then Methylene Chloride.

10.7 Concentrating the sample extracts.

10.7.1 Transfer the extract from the Erlenmeyer flask to a rinsed (7.2), 200 mL Turbovap tube being careful to avoid transferring any sodium sulfate, which can act as a boiling stone during concentration. Rinse the Erlenmeyer three times with methylene chloride, transferring the rinse to the Turbovap tube.

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10.7.2 Concentrate the samples to approximately 500 µL using the Turbovap II at 40°C with enough N_2 pressure to swirl, but not splash the extract in the tube. The pressure needed to cause the contents to swirl may change as the volume of solvent in the Zymark tube decreases.

10.8 Esterification Process.

10.8.1 Add approximately 1.5 mL diazomethane reagent to each sample tube. Swirl by hand for one minute. Allow to stand for 30+ minutes with occasional swirling. If the yellow color persists and no bubbles are being generated, the derivatization is complete. If the yellow color is not present, the diazald has been consumed and more must be added until the yellow color persists.

10.8.2 All samples in a batch must be derivatized with the same batch of diazomethane, since the efficiency of the derivatizing agent varies from batch to batch and decreases over time.

10.9 Final transfer: If the sample extract has not already concentrated down to 500ul through evaporation, reduce the sample volume to approximately 500 µL by allowing the solvent to evaporate spontaneously at room temperature to remove excess ether/diazomethane. Alternatively, use a slow stream of Nitrogen gas to concentrate the extract to approximately 500 µL in a water bath at 35°C. Using a 1 ml graduated pippet, bring up to a 1mL volume with methylene chloride and transfer sample to an amber GC vial and crimp for analysis.

11.0 CALCULATIONS:

11.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for all applicable calculations.

12.0 DATA REDUCTION & RECORDS:

12.1 All records must be completed at the time of sample preparation. Document all out of the ordinary information on the extraction worksheet such as a sample with high sediment content or strong odor.

12.2 Extraction paperwork is delivered to the analytical group and the samples are delivered to the GC/MS analyst or stored in the sample preparation laboratory refrigerator freezer door.

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12.3 Once the analysis is complete the GC/MS analyst electronically transfers the data into the LIMS, creates a data packet that includes all applicable forms and raw data and submits data to an authorized technical peer for data verification. Refer to the SOP GCMS8270MDAL2 for more detail.

13.0 REPORTING:

13.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for information regarding reporting.

14.0 QUALITY CONTROL:

14.1 Batch QC Frequency:

14.1.1 Batch QC generally consists of a MB, LCS, LCSD, MS and MSD with each set of 20 or fewer samples prepared together.

14.1.2 In situations when insufficient sample is received for MS and MSD a sample duplicate may be substituted for the MSD.

14.1.3 Each client sample and all QC samples are spiked with a surrogate solution to determine extraction efficiency.

14.2 Acceptance Limits for Batch QC:

14.2.1 Please refer to SOP GCMS8270MDAL2 for the batch QC limits.

14.3 Corrective Action for Batch QC:

14.3.1 If the MB, LCS, LCSD or the RPD between the LCS and LCSD are outside of acceptance limits then the batch must be re-extracted and reanalyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

14.3.2 If the MS/MSD, including the RPD between the MS/MSD is outside the acceptance limits then the data associated with the project from which that MS/MSD originated must be appropriately qualified. This assumes that the QC in 14.3.1 is within acceptance limits. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

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14.3.3 If the sample surrogates are outside of acceptance limits the specific sample must be re-extracted and re-analyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

15.0 METHOD PERFORMANCE:

15.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for all applicable method performance.

16.0 DETECTION LIMITS:

16.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for all applicable detection and reporting limits.

17.0 REFERENCES:

17.1 PRIMARY REFERENCES:

17.1.1 US EPA SW-846 Method 8151A.

17.2 SECONDARY REFERENCES:

17.2.1 US EPA SW-846 Method 3510C.

18.0 WASTE MANAGEMENT & POLLUTION PREVENTION:

18.1 Please refer to the general policies and procedures outlined in chapter 7 of the QAM regarding waste management and pollution prevention.

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Appendix A

Preparation Bench Sheet

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PREPARATION BENCH SHEET

B8J0429

Braun Intertec Corporation

Analysis: List 2 Water

Logbook:

Matrix: Water

Analyst: RDS

Printed: 4/2/2009 3:12:45PM

Prepared using: ENVSVOCGCMS - EPA 3510C

Surrogate ID: 8H13009

Lab Number	Prepared	Initial (mL)	Final (mL)	Spike ID	uL Spike	Source ID	uL Surrogate	Position	Extraction Comments
0806400-01	10/20/08 06:05	790	1				50		Run MS/MSD
B8J0429-BLK1	10/20/08 06:05	1000	1				50		
B8J0429-BS1	10/20/08 06:05	1000	1	8B25013	50		50		
B8J0429-BSD1	10/20/08 06:05	1000	1	8B25013	50		50		
B8J0429-MS1	10/20/08 06:05	740	1	8B25013	50	0806400-01	50		
B8J0429-MSD1	10/20/08 06:05	770	1	8B25013	50	0806400-01	50		

Reagent	Description
8B25013	MDA L2 spike std. 100UG/ML
8E16023	Acidified Sodium Sulfate
8H13009	MDA L2 Surrogate std. (DCAA)
8H27005	Diazomethane
8I11021	NaCl
8J03016	Methylene Chloride
8J06018	12 N H_2SO_4
8J06026	6N NaOH

UMP006681

Appendix B

Analytical Standard Record

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Analytical Standard Record

Braun Intertec Corporation

8L03026

Description:	MDA L2 Surrogate std. (DCAA)	Expires:	06/01/09
Standard Type:	Surrogate Spike	Prepared:	12/03/08
Solvent:	Acetone trace 6E05017	Prepared By:	Rupali Sawant
Final Volume (mls):	10	Department:	ENVSVOCGCMS
Vials:	1	Last Edit:	12/03/08 14:27 by RSS

MDA List 2 Surrogate Stock (2,4-Dichlorophenylacetic acid) 6G06018, 500ul diluted to 10ml with acetone

Analyte	CAS Number	Concentration	Units
D.C.A.A.	19719-28-9	100	ug/mL

Parent Standards used in this standard:

Standard	Description	Prepared	Prepared By	Expires	Last Edit	(mls)
7F06021	MDA LIST2 SURROGATE STOC	06/06/07	Jamie Ryan	04/01/09	07/11/07 11:09 by JLR	0.5

Reviewed By ____________________ Date ____________________

DESCRIPTION:

Sample Preparation for MDA List 1 Pesticides in Solid Sample Matrices using Solvent Extraction by Microwave.

SUMMARY:

This procedure is used to prepare solid samples for the analysis of MDA List 1 pesticides, organo-phosphorus, nitrogen-containing and triazine pesticides. This procedure is based on EPA Method SW-846 3546. A 15 gram sample is dried using diatomaceous earth and extracted with a 50% methylene chloride and 50% acetone mixture using the CEM Mars Xpress Microwave system. The sample extract is dried with sodium sulfate and concentrated to a 1 mL final volume using the Zymark TurboVap concentration station.

SCOPE:

This procedure complies with the requirements of the Resource Conservation and Recovery Act (RCRA). This SOP is applicable to the preparation of solid samples using microwave extraction.

DOCUMENT CONTINUITY:

This SOP is an original SOP.

SIGNATURES:

Quality Assurance [signature] **Date** 1/13/09
Michelle Hubanks

Technical Lead [signature] **Date** 1/8/09
Rebecca Bilek, Ph.D.

Laboratory Manager [signature] **Date** 01/09/09
Thomas P. Wagner

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1.0 PERSONNEL QUALIFICATIONS:

1.1 Personnel performing this procedure must be qualified per the requirements outlined in chapter 1 of the Analytical Laboratory Quality Assurance Manual (QAM).

2.0 SAFETY:

2.1 Personnel performing this procedure must follow general laboratory safety practices as defined in chapter 1 of the (QAM).

2.2 When working with organic compounds, wear solvent resistant gloves.

2.3 Follow standard laboratory safety procedures. Always wear a lab coat and safety glasses.

2.4 Review all Material Safety Data Sheets for chemicals used in this procedure.

3.0 DEFINITIONS:

3.1 Refer to standardized Braun Intertec Corporation definitions as described in chapter 4 of the QAM.

3.2 TurboVap tubes: Zymark TurboVap 200 mL concentration tubes.

3.3 $MeCl_2$: Methylene Chloride

3.4 UPDI: Ultra Pure Deionized Water

4.0 FORMS & RECORDS:

4.1 LIMS Bench Sheet, Refer to Appendix A.

4.2 LIMS Standard Record, Refer to Appendix B.

5.0 EQUIPMENT & SUPPLIES:

5.1 CEM MARS5 Xpress Accelerated Reaction System, Model #907501, including solvent sensor assembly installed in exhaust line.

5.1.1 MARS Xpress Vessels, 75mL with stoppers and caps.

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5.1.2 Vessel turntable, 40 position with composite sleeves for each position.

5.1.3 MARS Xpress vessel capping station.

5.1.4 Computer with Synergy Prep Software, version 3.32.

5.1.5 Microwave vessel racks.

5.1.6 Turntable assembly and filter funnels for filtering extract.

5.2 Graduated pipets.

5.3 Crimp top vials and PTFE crimp caps.

5.4 Zymark TurboVap Concentration Station.

5.5 Zymark TurboVap 200 mL Concentration tubes.

5.6 Beakers, 50 mL.

5.7 Erlenmeyer flasks, 250 mL.

5.8 Analytical balance.

5.9 Filter paper, porosity: coarse, flow rate: fast, diameter: 18.5 cm (Fisher 0-790-G, or equivalent).

5.10 Powder funnels.

6.0 REAGENTS & STANDARDS:

6.1 Ultra Pure Deionized Water (UPDI)

6.2 Sodium Sulfate, 10-60 mesh, anhydrous (Fisher Scientific, Cat. #S415-200, or equivalent), purified by heating to 450°C for two hours.

6.3 Diatomaceous earth (ICN Biomedicals, Inc., Cat #157606, or equivalent), purified by heating to 450°C for two hours.

6.4 Methylene Chloride, pesticide grade (Mallinckrodt, Cat. #H485-10, or equivalent).

6.5 Acetone, pesticide grade (Fisher Scientific, Cat. #A40-4, or equivalent).

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6.6 Ottawa Sand (Fisher Scientific, Cat. #S23-3, or equivalent).

6.7 Surrogate Solution – 100 μg/mL of Atrazine-d5 and Diazinon-d10: Prepare surrogate by adding the appropriate amount of Diazinon-d10 and Atrazine-d5 stock solution to 10 mL final volume of acetone to achieve 100 μg/mL. Record standard preparation in the LIMS.

6.8 Spike Solution – 20 μg/mL of MDA list 1 spike mix: Prepare by adding 1000 μL of 500 μg/mL MDA List 1 stock standard to a 25 mL final volume of acetone in a volumetric flask. Additional analytes may be added as necessary at varying concentrations. Record standard preparation in the LIMS.

7.0 INTERFERENCES & PROCEDURAL LIMITATIONS:

7.1 Rinse all glassware with $MeCl_2$ before use to ensure glassware is clean and free from contaminants.

7.2 Refer to SOP GCMS8270MDAL1 for analytical interferences.

8.0 SAMPLE ACCEPTANCE & HOLDING TIMES:

8.1 Samples must be stored at 4°C from the time of collection to the time of extraction.

8.2 Samples must be extracted within 14 days of sample collection and analyzed within 40 days of extraction.

9.0 CALIBRATION & STANDARDIZATION:

9.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for the calibration and standardization of the GC/MS.

10.0 PROCEDURE:

10.1 Record standard preparation in Element if new standards are needed.

10.1.1 Under Laboratory, click on Standards. Click Add.

10.1.2 For parent standards choose 1. "Specify each analyte and its concentration". Fill in the description, department, expiration date, initials and prepared date. Lot number and additional standard information can be typed in the comment section.

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10.1.3 Choose the analytes from the analyte list. To narrow the list, select 8270 MDA List 1 Soils. Select the appropriate compounds from the list and add them to the standard.

10.1.4 Adjust the concentration and the concentration units as necessary.

10.1.5 Make sure the standard type is appropriate (i.e. for spike, click spike. For surrogate, click surrogate).

10.1.6 To prepare child standards click Add and choose 2. "Combine and/ or dilute existing standards."

10.1.7 Fill in the header information and choose the appropriate parent standard(s). Entering the standard volumes and the final volume will adjust the concentration of the child standard. It will not appear until the standard is saved.

10.1.8 Again, make sure the standard type is appropriate.

10.1.9 For standards that are created new but exactly the same as previous standards instead of choosing add, choose copy. The standard can be copied so that the analytes and concentrations do not need to be added. Fill in the header information with the correct preparation date and expiration date.

10.2 Create a new batch/bench sheet in Element.

10.2.1 Under Laboratory, click Batch. Click Add to create a new batch.

10.2.2 Choose the preparation method (EPA 3546), matrix and surrogate. Make sure the surrogate type is pre-prep. In the reagent box, right click and choose the appropriate solvents and reagents used for traceability.

10.2.3 Choose the appropriate analysis and click bench sheet.

10.2.4 On the bench sheet click edit and then add. Choose client samples (by container). Choose all of the samples that will be prepared in that batch. There cannot be more than 20 samples in each batch.

10.2.5 With each batch a BLK1, BS1, BSD1, MS1, MSD1 will be added. If there is insufficient sample for a MS/MSD pair a sample duplicate can be substituted. To remove QC or samples click on the appropriate sample and

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choose remove. To add QC click add and choose the appropriate QC sample.

10.2.6 To add information such as initial weight and final volumes, prepared date, prepared by and comments, highlight samples or QC, right click and choose the appropriate command. Be sure to adjust the sample volume to document the actual sample volume used in extraction.

10.2.7 The LCS/LCSD/MS/MSD standard ID can be added by right clicking on QC sample and choosing the appropriate command. Also fill in the standards type (pre-prep) and the amount spiked. For sample duplicates and MS/MSD the sample source must also be added.

10.2.8 Print the bench sheet using the bch_std06.00.rpt.

10.3 All glassware (50 mL beakers, 250 mL Erlenmeyer flasks and TurboVap tubes) must be rinsed three times with $MeCl_2$ prior to extraction.

10.4 Solvent rinse microwave extraction vessels once with $MeCl_2$.

10.5 Prepare samples for extraction.

10.5.1 Weigh approximately 15 grams of each sample into a 50 mL beaker. Document the actual sample weight on the bench sheet.

10.5.2 For laboratory control samples (LCS/LCSD/BLK) use 15 grams of Ottawa sand.

10.5.3 Deliver 100 µL MDA List 1 surrogate to all samples, including quality control samples.

10.5.4 Deliver 500 µL MDA List 1 spike to the LCS/LCSD and MS/MSD.

10.5.5 Mix with diatomaceous earth until free flowing to absorb moisture from the sample. In order to achieve optimal recoveries, it is important to make sure the sample is free flowing.

10.5.6 Add 5 g of solid sodium sulfate to each sample (including QC samples) and mix.

10.5.7 Pour the sample mixed with diatomaceous earth and sodium sulfate into the vessel using a powder funnel. Organize vessels in the vessel rack and make a note of the position of each in the rack.

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10.5.8 Dispense 15 mL of $MeCl_2$ into the beaker after the soil has been transferred to rinse the beaker. Add the rinsing solvent to the vessel using the powder funnel, rinsing the funnel as the solvent is added. Repeat with 15 mL of acetone.

10.6 Stopper and cap each vessel. Start the cap by hand to make sure the threads are aligned correctly and finish using the Vessel Capping Station, which will result in all vessels being capped uniformly. Shake each vessel well to mix the contents.

10.7 Put the vessels in the turntable, labeling the turntable position of each on the bench sheet. It is important to distribute the vessels around the turntable instead of bunching them all together.

10.8 Load the turntable containing the microwave vessels into the microwave. The turntable will lock in place when aligned correctly.

10.9 Select the method in the CEM Synergy Prep software for organic extraction based on the number of vessels that will be processed together. For 6 to 10 vessels, select the method “400 Org Extraction”, for 11 to 20 vessels use “800 Org Extraction”, and for more than 20 vessels use “1600 Org Extraction”. All of the methods are identical except for the power (in watts).

10.9.1 The required parameters for the extraction of organic compounds from soil samples are listed in Table 1 below.

Table 1: Extraction Parameters

Parameters	**MDA list 1**
Control style	Ramp to Temperature
Vessel type	Xpress
Reaction type	organic
Power (watts)	400, 800, or 1600
%Power	100
Time to ramp to temperature	10:00 minutes
Temperature	110°C
Hold time	20:00 minutes

10.9.2 After the correct method is selected in the software, click “run method” or “start”.

10.10 Allow the vessels to cool completely (inside or outside the unit) before proceeding.

10.11 Collection, filtering, drying, and concentration of sample extracts.

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10.11.1 After the vessels are at room temperature, remove each from the turntable and organize in the vessel rack. While transferring the vessels to the rack, shake the vessel to loosen the soil. This will aid in transferring the contents.

10.11.2 Use the vessel capping station in reverse mode to loosen each vessel cap.

10.11.3 Decant the liquid portion in each vessel into a filter assembly consisting of a 250 mL Erlenmeyer flask (rinsed with $MeCl_2$), positioned in the turntable with a filter funnel over the mouth and a piece of filter paper (folded into eighths) inside the funnel.

10.11.4 Wait until after the extract has almost finished passing through the filter before adding the soil sample to avoid splashing. Rinse the vessel with two 15mL portions of $MeCl_2$, using each to rinse the soil in the filter paper of residual analytes.

10.11.5 Add a 15 mL portion of $MeCl_2$ directly to the filter to again rinse the soil sample.

10.11.6 When all of the solvent has passed through the filter paper into the flask, add sodium sulfate to dry the extract.

10.11.7 Rinse the appropriate number of TurboVap tubes with methylene chloride.

10.11.8 Label the TurboVap tubes with the appropriate sample ID.

10.11.9 Decant the sample extract into the tube, rinsing the flask three times with methylene chloride, combining all rinses into the TurboVap tube. Take care not to get any sodium sulfate in the TurboVap tube.

10.12 Concentrate the extracts down to just below 1 mL in the TurboVap tube. Add $MeCl_2$ drop wise to bring back up to a final volume of 1 mL with a graduated pipet. Quantitatively transfer 1 mL of the extract into a labeled amber autosampler vial and crimp top.

11.0 CALCULATIONS:

11.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for all applicable calculations.

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12.0 DATA REDUCTION & RECORDS:

12.1 Complete a Track-IT! if required and route to QA/QC.

12.2 Once the analysis is complete the GC/MS analyst electronically transfers the data into the LIMS, creates a data packet that includes all applicable forms and raw data and submits data to an authorized technical peer for data verification. Refer to the SOP GCMS8270MDAL1 for more detail.

12.3 All records must be completed at the time of sample preparation. Document all out of the ordinary information on the extraction worksheet such as a sample with a strong odor.

12.4 Extraction paperwork is delivered to the analytical group and the samples are delivered to the GC/MS analyst or stored in the sample preparation laboratory refrigerator freezer door.

13.0 REPORTING:

13.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for information regarding reporting.

14.0 QUALITY CONTROL:

14.1 Batch QC Frequency:

14.1.1 Batch QC generally consists of a BLK, LCS, LCSD, MS and MSD with each set of 20 or fewer samples prepared together.

14.1.2 In situations when insufficient sample is received for MS and MSD a sample duplicate may be substituted for the MSD.

14.1.3 Each sample, including QC samples, is spiked with a surrogate solution to determine extraction efficiency.

14.2 Acceptance Limits for Batch QC:

14.2.1 Please refer to SOP GCMS8270MDAL1 for the batch QC limits.

14.3 Corrective Action for Batch QC:

14.3.1 If the BLK, LCS, LCSD or the RPD between the LCS and LCSD are outside of acceptance limits then the batch must be re-extracted and

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reanalyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of acceptance limits a Track-IT! must be completed and routed to QA/QC.

14.3.2 If the MS/MSD, including the RPD between the MS/MSD is outside the acceptance limits then the data associated with the project from which that MS/MSD originated must be appropriately qualified. This assumes that the QC in 14.3.1 is within acceptance limits. If any of the QC is outside of acceptance limits a Track-IT! must be completed and routed to QA/QC.

14.3.3 If the sample surrogates are outside of acceptance limits the specific sample must be re-extracted and re-analyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of acceptance limits a Track-IT! must be completed and routed to QA/QC.

15.0 METHOD PERFORMANCE:

15.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for all applicable method performance.

16.0 DETECTION LIMITS:

16.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for all applicable detection and reporting limits.

17.0 REFERENCES:

17.1 PRIMARY REFERENCES:

17.1.1 US EPA SW-846 Method 3546

18.0 WASTE MANAGEMENT & POLLUTION PREVENTION:

18.1 Please refer to the general policies and procedures outlined in chapter 7 of the QAM regarding waste management and pollution prevention.

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Appendix A

Preparation Bench Sheet

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PREPARATION BENCH SHEET

B9A0089

Braun Intertec Corporation

Analysis: MDA LIST 1 MICROWAVE IDCs

Logbook:

Matrix: Soil

Prepared using: ENVSVOCGCMS - EPA 3546

Analyst: RUPALI

Printed: 1/8/2009 3:34:59PM

Surrogate ID: 8K20007

Lab Number	Prepared	Initial (g)	Final (mL)	Spike ID	uL Spike	Source ID	uL Surrogate	Position	Extraction Comments
0900079-01	01/08/09 10:55	15.8	1				100		Rupali Microwave IDC#4,500ul of #8L17026 added
0900079-02	01/08/09 10:55	15.25	1				100		Rupali Microwave IDC#4,500ul of #8L17026 added
0900079-03	01/08/09 10:55	15.34	1				100		Rupali Microwave IDC#4,500ul of #8L17026 added
0900079-04	01/08/09 10:55	15.44	1				100		Rupali Microwave IDC#4,500ul of #8L17026 added
B9A0089-BLK1	01/08/09 10:55	15.25	1				100		

Reagent	Description
8H07002	Diatomaceous Earth
8H14004	Sodium Sulfate
8H22033	Ottawa Sand
8K11005	Acetone Pesticide Grade
8K20007	MDA List 1 Surrogate 100 ug/mL
9A07032	Methylene Chloride

Appendix B

Analytical Standard Record

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Analytical Standard Record

Braun Intertec Corporation

8L17026

Description:	MDA L1 SPIKE SOLN, 20ug/ml	Expires:	06/07/09
Standard Type:	Analyte Spike	Prepared:	12/17/08
Solvent:	8K11005	Prepared By:	Robert D. Schmidt
Final Volume (mls):	10	Department:	ENVSVOCGCMS
Vials:	1	Last Edit:	12/17/08 15:06 by RDS

400ul stock diluted to 10 ml with acetone

Sonicate stock before making spike.

Analyte	CAS Number	Concentration	Units
Acetochlor	34256-82-1	20	ug/mL
Alachlor	15972-60-8	20	ug/mL
Atrazine	1912-24-9	20	ug/mL
Chlorpyrifos	2921-88-2	20	ug/mL
Cyanazine	21725-46-2	20	ug/mL
Deisopropylatrazine	1007-28-9	20	ug/mL
Desethylatrazine	6190-65-4	20	ug/mL
Dimethenamid	87674-68-8	20	ug/mL
EPTC	759-94-4	20	ug/mL
Ethalfluralin	55283-68-6	20	ug/mL
Fonofos	944-22-9	20	ug/mL
Metolachlor	51218-45-2	20	ug/mL
Metribuzin	21087-64-9	20	ug/mL
Pendimethalin	40487-42-1	20	ug/mL
Phorate	298-02-2	20	ug/mL
Prometon	1610-18-0	20	ug/mL
Propachlor	1918-16-7	20	ug/mL
Propazine	139-40-2	20	ug/mL
Simazine	122-34-9	20	ug/mL
Terbufos	13071-79-9	20	ug/mL
Triallate	2303-17-5	20	ug/mL
Trifluralin	1582-09-8	20	ug/mL

Parent Standards used in this standard:

Standard	Description	Prepared	Prepared By	Expires	Last Edit	(mls)
8F09038	MDA L1 STOCK 500 ug/mL	06/09/08	** Vendor **	06/07/09	06/09/08 13:20 by NPL	0.4

Reviewed By ______________________ Date

UMP006697

DESCRIPTION:

Sample Preparation for MDA list 1 Pesticides in Aqueous Sample Matrices.

SUMMARY:

This procedure is used to prepare aqueous samples for the analysis of MDA list 1 pesticides, organo-phosphorus, nitrogen-containing and triazine pesticides. This procedure is based on EPA Method SW-846 3520C. A Rot-x-tract continuous liquid/liquid extractor/evaporator is cycled for a minimum of 18 hours to isolate organic compounds from the water matrix using methylene chloride solvent. The extract is concentrated to a 1 mL final volume.

SCOPE:

This procedure complies with the requirements of the Resource Conservation and Recovery Act (RCRA). This SOP is applicable to the preparation of aqueous samples using continuous liquid-liquid extraction.

DOCUMENT CONTINUITY:

This SOP replaces MDA1H2OPREP Revision 1.

SIGNATURES:

Quality Assurance ________________ **Date** 4/16/09
Michelle Hubanks

Technical Lead ________________ **Date** 04/15/2009
Rupali Sawant

Laboratory Manager ________________ **Date** 04/16/2009
Thomas P. Wagner

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1.0 PERSONNEL QUALIFICATIONS:

1.1 Personnel performing this procedure must be qualified per the requirements outlined in chapter 1 of the Analytical Laboratory Quality Assurance Manual (QAM).

2.0 SAFETY:

2.1 Personnel performing this procedure must follow general laboratory safety practices as defined in chapter 1 of the (QAM).

2.2 When working with organic compounds, wear solvent resistant gloves.

2.3 Follow standard laboratory safety procedures. Always wear a lab coat and safety glasses.

2.4 Review all Material Safety Data Sheets for chemicals used in this procedure.

3.0 DEFINITIONS:

3.1 Refer to standardized Braun Intertec Corporation definitions as described in chapter 4 of the QAM.

3.2 PTFE: polytetrafluoroethylene.

3.3 UPDI: Ultra Pure Deionized Water

3.4 $MeCl_2$: Methylene Chloride.

3.5 LIMS: Laboratory Information Management System.

3.6 Element: the LIMS used by the Analytical Laboratory.

4.0 FORMS & RECORDS:

4.1 LIMS Bench Sheet, Refer to Appendix A.

4.2 LIMS Standard Record, Refer to Appendix B.

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5.0 EQUIPMENT & SUPPLIES:

5.1 Rot-x-tract liquid/liquid extractor/evaporator (Organomation). Set-up includes water bath, stand, cover disk, condenser holder/water manifold assembly, rotating water manifold, clamp assembly, tubing and connectors.

5.2 Corning Accelerated One-Step glassware (Organomation). Each set includes One Step body, Curved Snyder column, in-line K-D Concentrator Tube- vacuum insulated, ceramic support ring, 45 degree glass cup and o-ring for membrane coupler, Teflon sleeve and Teflon tubing with stopcock.

5.3 Hydrophobic membrane.

5.4 Teflon boiling grids.

5.5 Various clips to hold glassware together.

5.6 pH paper – wide range 0-14.

5.7 Autosampler 2 mL vials and crimp aluminum seals.

5.8 Graduated cylinder – 1 Liter

5.9 Glass stir rod.

5.10 Gas tight syringes

6.0 REAGENTS & STANDARDS:

6.1 Ultra Pure Deionized water equivalent to ASTM type 1.

6.2 Methylene Chloride, Pesticide grade or equivalent.

6.3 Surrogate Solution – 100 µg/mL of Atrazine-d5 and Diazinon-d10: Prepare surrogate by diluting the appropriate amount of Diazinon-d10 and Atrazine-d5 stock solution to 10 mL final volume of acetone to achieve 100 µg/mL. Record standard preparation in the LIMS.

6.4 Spike Solution – 20 µg/mL of MDA list 1 spike mix: Prepare by diluting 1000 µL of 500 µg/mL MDA List 1 stock standard to a 25 mL final volume of acetone in a volumetric flask. Additional analytes may be added as necessary at varying concentrations. Record standard preparation in the LIMS.

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6.5 Sodium hydroxide solution (10N), NaOH. Dissolve 40g NaOH in organic-free reagent water and dilute to 100mL. Other concentrations of hydroxide solutions may be used to adjust sample pH, provided that the volume does not appreciably change the total volume.

6.6 Sulfuric acid solution (1:1 v/v) H_2SO_4. Slowly add 50mL of H_2SO_4 to 50 mL of organic-free reagent water. Other concentrations of acid solutions may be used to adjust sample pH, provided that the volume added does not appreciably change the total sample volume.

7.0 INTERFERENCES & PROCEDURAL LIMITATIONS:

7.1 Rinse all glassware with $MeCl_2$ before use to ensure glassware is clean and free from contaminants.

7.2 The temperature of the water bath is critical to the efficiency of the extraction. The water bath must be maintained at 70°C for the entire extraction procedure.

7.3 The flow rate from the cooling water is critical to the efficiency of the extraction. The flow rate must be in the 2500 cc/min range for the condensers and 3 cc/min for the water bath. The condensers must feel cold to the touch.

8.0 SAMPLE ACCEPTANCE & HOLDING TIMES:

8.1 Samples must be stored at 4°C from the time of collection to the time of extraction.

8.2 Samples must be extracted within 7 days of sample collection and analyzed within 40 days of extraction.

9.0 CALIBRATION & STANDARDIZATION:

9.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for the calibration and standardization of the GC/MS.

10.0 PROCEDURE:

10.1 Record standard preparation in Element if new standards are needed.

10.1.1 Under Laboratory, click on Standards. Click Add.

10.1.2 For parent standards choose 1. "Specify each analyte and its concentration". Fill in the description, department, expiration date, initials and prepared date.

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Lot number and additional standard information can be typed in the comment section.

10.1.3 Choose the analytes from the analyte list. To narrow the list, select 8270 MDA List 1 Waters. Select the appropriate compounds from the list and add them to the standard.

10.1.4 Adjust the concentration and the concentration units as necessary.

10.1.5 Make sure the standard type is appropriate (i.e. for spike, click spike. For surrogate, click surrogate).

10.1.6 To prepare child standards click Add and choose 2. "Combine and/ or dilute existing standards."

10.1.7 Fill in the header information and choose the appropriate parent standard(s). Entering the standard volumes and the final volume will adjust the concentration of the child standard. It will not appear until the standard is saved.

10.1.8 Again, make sure the standard type is appropriate.

10.1.9 For standards that are created new but exactly the same as previous standards instead of choosing add, choose copy. The standard can be copied so that the analytes and concentrations do not need to be added. Fill in the header information with the correct preparation date and expiration date.

10.2 Create a new batch/bench sheet in Element.

10.2.1 Under Laboratory, click Batch. Click Add to create a new batch.

10.2.2 Choose the preparation method, matrix and surrogate. Make sure the surrogate type is pre-prep. In the reagent box, right click and choose the appropriate solvents and reagents used for traceability.

10.2.3 Choose the appropriate analysis and click bench sheet.

10.2.4 On the bench sheet click edit and then add. Choose client samples (by container). Choose all of the samples that will be prepared in that batch. There cannot be more than 20 samples in each batch.

10.2.5 With each batch a MB, BS1, BSD1, MS1, MSD1 will be added. If there is insufficient sample for a MS/MSD pair a sample duplicate can be substituted.

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To remove QC or samples click on the appropriate sample and choose remove. To add QC click add and choose the appropriate QC sample.

10.2.6 To add information such as initial and final volumes, prepared date, prepared by and comments, highlight samples or QC, right click and choose the appropriate command. Be sure to adjust the sample volume to document the actual sample volume used in extraction.

10.2.7 The LCS/LCSD/MS/MSD standard ID can be added by right clicking on each QC sample and choosing the appropriate command. Also fill in the standards type (pre-prep) and the amount spiked. For sample duplicates and MS/MSD the sample source must also be added.

10.2.8 Print the bench sheet using the bch_std06.00.rpt.

10.3 Turn on the water bath and allow the temperature to reach 70°C prior to use.

10.4 Turn on the cooling water to the condensers. Confirm flow rates and ensure that the condensers feel cold to the touch prior to use.

10.5 Prepare glassware for extraction.

10.5.1 All extraction glassware must be rinsed with methylene chloride prior to extraction.

10.5.2 Check the extraction body base for chips. If there are any chips along the bottom edge you will not get a perfect seal and there will be a loss of sample.

10.5.3 Assemble the extraction body, the coupler, the ceramic support rings and the membrane into one piece. Inspect the membrane for any tears, wrinkles or thin spots. Discard membrane if any are present.

10.5.4 Start to close the coupler and then slide the extractor body into the coupler and tighten the coupler to hand tight. Make sure that the side port for the Snyder column at the top lines up with the base valve assembly. Close the valve on the coupler to keep any sample from leaking out when it is poured into the body.

10.5.5 Assemble the K-D concentrator tube, boiling grid, and the curved Snyder column. Set this aside until after the sample has been spiked with surrogate and for QC samples with surrogate and spike.

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10.5.6 Label the extraction body with the type of analysis and the sample number for each sample being extracted. Include all batch quality control samples.

10.6 Prepare sample for extraction.

10.6.1 Check the pH of each sample with pH paper and record on the bench sheet. The pH of the sample must be between 5 and 7 units. Using NaOH or H_2SO_4 dropwise, adjust the pH of any sample that is not between 5 and 7 units. Note in the comments section of the bench sheet that the pH was adjusted.

10.6.2 Measure the volume of each sample by transferring it first into a 1-liter graduated cylinder before pouring it into extraction body. Alternatively, the volume of the sample being extracted may be measured by marking the water meniscus on the side of the sample bottle for later determination of the sample volume. The volume may be measured by filling a graduated cylinder, then pouring water into the sample jar to the mark. The difference in the volume in the graduated cylinder is the volume of sample used. Read the volume to the nearest 5 mL and record the volume on the bench sheet.

10.6.3 Carefully pour the sample into the extraction body. If the sample has suspended solids or if the sample has sludge/sediment, do not allow this into the body. The particles will block the membrane and the extraction will not be complete.

10.6.4 Be aware that any oily samples will go right into the solvent layer and produce a higher volume in the K-D and boil up in the Snyder column. In this case, you may want to use less than 1 liter for oily samples or contact the project manager.

10.6.5 For laboratory control samples (LCS/LCSD/MB) use 1 L of UPDI water as the control matrix.

10.6.6 Deliver 100 µL MDA list 1 surrogate to all samples, including quality control samples.

10.6.7 Deliver 500 µL MDA list 1 spike to the LCS/LCSD and MS/MSD.

10.7 Continue assembling extraction apparatus.

10.7.1 Attach the K-D/Concentrator apparatus to the extraction body. Make sure that the metal joint clamp is tightened to keep methylene chloride from leaking out.

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10.7.2 Install the entire apparatus into the preheated water bath. Pump 100 mL of methylene chloride through the condenser to fall down into the extraction body. Open the valve on the coupler to allow the methylene chloride through the membrane to start the extraction.

10.8 Allow the methylene chloride to cycle for at least 18 hours.

10.8.1 Note the temperature, pH, start time and date of the extraction on the bench sheet. Later, when the 18 hours or more of the extraction cycling is complete, record the temperature, end time and date of the extraction on the bench sheet.

10.8.2 Observe each extractor to ensure that the methylene chloride is cycling and that the Snyder column is "chattering".

10.8.3 If an emulsion is present the methylene chloride will back up, remaining in the extraction body. The analyst must employ mechanical techniques to complete the phase separation, typically with a glass stir rod. The analyst must be careful when stirring to avoid damaging the membrane.

10.9 Concentrate and collect sample extract.

10.9.1 After the 18 hours has elapsed, shut off the valve on the coupler. Continue to heat the samples until the Synder column stops chattering, approximately 15-30 minutes. Lable and separate the bottom 2 pieces of glassware from the snyder column. Put these back into the water bath to finish evaporating.

10.9.2 Remove the set-up from the water bath and allow it to cool, when the volume in the concentrater tube is 1 ml. The bath and the water can be turned off.

10.9.3 Remove the boiling grid. Quantitatively transfer the 1 mL extract to an amber autosampler vial and crimp for analysis.

10.10 Drain off the methylene chloride from the extraction body into a waste container. The remaining sample is then poured down the drain. All glassware, excluding the Snyder columns, is then washed in the Miele dishwasher.

11.0 CALCULATIONS:

11.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for all applicable calculations.

12.0 DATA REDUCTION & RECORDS:

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12.1 Once the analysis is complete the GC/MS analyst electronically transfers the data into the LIMS, creates a data packet that includes all applicable forms and raw data and submits data to an authorized technical peer for data verification. Refer to the SOP GCMS8270MDAL1 for more detail.

12.2 All records must be completed at the time of sample preparation. Document all out of the ordinary information on the bench sheet such as a sample with high sediment content or strong odor.

12.3 Extraction paperwork is delivered to the analytical group and the samples are delivered to the GC/MS analyst or stored in the sample preparation laboratory refrigerator freezer door.

13.0 REPORTING:

13.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for information regarding reporting.

14.0 QUALITY CONTROL:

14.1 Batch QC Frequency:

14.1.1 Batch QC generally consists of a MB, LCS, LCSD, MS and MSD with each set of 20 or fewer samples prepared together.

14.1.2 In situations when insufficient sample is received for MS and MSD a sample duplicate may be substituted for the MSD.

14.1.3 Each sample, including QC samples, is spiked with a surrogate solution to determine extraction efficiency.

14.2 Acceptance Limits for Batch QC:

14.2.1 Please refer to SOP GCMS8270MDAL1 for the batch QC limits.

14.3 Corrective Action for Batch QC:

14.3.1 If the MB, LCS, LCSD or the RPD between the LCS and LCSD are outside of acceptance limits then the batch must be re-extracted and reanalyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

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14.3.2 If the MS/MSD, including the RPD between the MS/MSD is outside the acceptance limits then the data associated with the project from which that MS/MSD originated must be appropriately qualified. This assumes that the QC in 14.3.1 is within acceptance limits. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

14.3.3 If the sample surrogates are outside of acceptance limits the specific sample must be re-extracted and re-analyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

15.0 METHOD PERFORMANCE:

15.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for all applicable method performance.

16.0 DETECTION LIMITS:

16.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for all applicable detection and reporting limits.

17.0 REFERENCES:

17.1 <u>PRIMARY REFERENCES:</u>

17.1.1 US EPA SW-846 Method 3520C

18.0 WASTE MANAGEMENT & POLLUTION PREVENTION:

18.1 Please refer to the general policies and procedures outlined in chapter 7 of the <u>QAM</u> regarding waste management and pollution prevention.

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Appendix A

Preparation Bench Sheet

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PREPARATION BENCH SHEET

B8K0430

Braun Intertec Corporation

Analysis: List 1 Water

Logbook:

Matrix: Water

Analyst: RDS

Printed: 4/2/2009 3:03:44PM

Prepared using: ENVSVOCGCMS - EPA 3520C

Surrogate ID: 8K20007

Lab Number	Prepared	Initial (mL)	Final (mL)	Spike ID	uL Spike	Source ID	uL Surrogate	Position	Extraction Comments
0807201-01	11/24/08 06:51	820	1				100		
0807201-02	11/24/08 06:51	830	1				100		
0807201-03	11/24/08 06:51	810	1				100		
0807201-04	11/24/08 06:51	755	1				100		MS/MSD
0807201-05	11/24/08 06:51	920	1				100		
B8K0430-BLK1	11/24/08 06:51	1000	1				100		
B8K0430-BS1	11/24/08 06:51	1000	1	8J29045	500		100		
B8K0430-BSD1	11/24/08 06:51	1000	1	8J29045	500		100		
B8K0430-MS1	11/24/08 06:51	810	1	8J29045	500	0807201-04	100		
B8K0430-MSD1	11/24/08 06:51	820	1	8J29045	500	0807201-04	100		

Reagent	Description
8J24001	Methylene Chloride
8J29045	MDA L1 SPIKE SOLN, 20ug/ml
8K20007	MDA List 1 Surrogate 100 ug/mL

Appendix B

Analytical Standard Record

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Analytical Standard Record

Braun Intertec Corporation

9B05039

Description:	MDA L1 SPIKE SOLN, 20ug/ml	Expires:	06/07/09
Standard Type:	Analyte Spike	Prepared:	02/05/09
Solvent:	8K11005	Prepared By:	Robert D. Schmidt
Final Volume (mls):	10	Department:	ENVSVOCGCMS
Vials:	1	Last Edit:	02/05/09 13:58 by RDS

400ul stock diluted to 10 ml with acetone

Sonicate stock before making spike.

Analyte	CAS Number	Concentration	Units
Metolachlor	51218-45-2	20	ug/mL
Alachlor	15972-60-8	20	ug/mL
Atrazine	1912-24-9	20	ug/mL
Chlorpyrifos	2921-88-2	20	ug/mL
Cyanazine	21725-46-2	20	ug/mL
Deisopropylatrazine	1007-28-9	20	ug/mL
Desethylatrazine	6190-65-4	20	ug/mL
Dimethenamid	87674-68-8	20	ug/mL
EPTC	759-94-4	20	ug/mL
Acetochlor	34256-82-1	20	ug/mL
Fonofos	944-22-9	20	ug/mL
Trifluralin	1582-09-8	20	ug/mL
Metribuzin	21087-64-9	20	ug/mL
Pendimethalin	40487-42-1	20	ug/mL
Phorate	298-02-2	20	ug/mL
Prometon	1610-18-0	20	ug/mL
Propachlor	1918-16-7	20	ug/mL
Propazine	139-40-2	20	ug/mL
Simazine	122-34-9	20	ug/mL
Terbufos	13071-79-9	20	ug/mL
Triallate	2303-17-5	20	ug/mL
Ethalfluralin	55283-68-6	20	ug/mL

Parent Standards used in this standard:

Standard	Description	Prepared	Prepared By	Expires	Last Edit	(mls)
8F09038	MDA L1 STOCK 500 ug/mL	06/09/08	** Vendor **	06/07/09	06/09/08 13:20 by NPL	0.4

Reviewed By ______________________ Date

DESCRIPTION:

Determination of MN Department of Agriculture List 2 (MDA2) Pesticides in Aqueous and Solid Samples by Gas Chromatography/Mass Spectrometry (GC/MS).

SUMMARY:

Prior to analysis, samples should be prepared using an appropriate sample preparation method. Water samples are prepared according to EPA SW-846 Method 8151B and EPA SW-846 Method 3510C. Soil samples are prepared according to EPA SW-846 Method 8151B and EPA SW-846 Methods 3545 and 3510C. This SOP is applicable to the analysis of all liquid and solid matrices for List 2 compounds. Qualitative identification of the components in the extract is performed by comparison of the retention time and mass spectra with that of a reference standard. Quantitative analysis is performed using the integrated area abundance of the extracted ion current profile (EICP) of the primary characteristic ion for each target analyte, relative to that of an internal standard.

SCOPE:

This procedure is based on US EPA SW-846 Method 8270C for extractable semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS). This method is used to determine the concentration of semivolatile organic compounds that are amenable to GC/MS in extracts prepared from all types of solid waste matrices, soils and ground water. The Minnesota Department of Agriculture List 2 (MDA2) pesticide compound list is routinely analyzed. This procedure complies with the requirements of the Resource Conservation and Recovery Act (RCRA) and the Minnesota Department of Agriculture Incident Response Program. This SOP applies to the analysis portion only. Please refer to MDA2H2OPREP and MDA2SOILPREP SOPs for the sample preparation procedures.

DOCUMENT CONTINUITY:

This document replaces Braun Intertec Corporation SOP GCMS8270MDAL2 Revision 2.

SIGNATURES:

Quality Assurance ______________________ **Date** 5/11/09
Michelle Hubanks

Technical Lead ______________________ **Date** 5/5/09
Mike Frencl

Laboratory Manager ______________________ **Date** 05/11/09
Thomas P. Wagner

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1.0 PERSONNEL QUALIFICATIONS:

1.1 Personnel performing this procedure must be qualified per the requirements outlined in chapter 1 of the Analytical Laboratory Quality Assurance Manual (QAM).

2.0 SAFETY:

2.1 Personnel performing this procedure must follow general laboratory safety practices as defined in chapter 1 of the QAM.

2.2 Review all Material Safety Data Sheets (MSDS) for chemicals used in this procedure.

2.3 Wear solvent-resistant gloves when working with samples, extracts, and solvents.

2.4 Work under a fume hood when extracting samples, preparing dilutions or making standards.

3.0 DEFINITIONS:

3.1 Refer to standardized Braun Intertec Corporation definitions as described in chapter 4 of the QAM.

3.2 QAM: Braun Intertec Corporation Analytical Laboratory Quality Assurance Manual.

3.3 QA/QC: Refers to the Quality Group (Quality Director and QA Officer).

3.4 LIMS: Laboratory Information Management System.

3.5 Element: The LIMS used by the Analytical Laboratory.

4.0 FORMS & RECORDS:

4.1 LIMS Bench Sheet, Refer to Appendix A.

4.2 LIMS Standard Record, Refer to Appendix B.

4.3 GC/MS SVOC Run Log, Refer to Appendix C.

4.4 LIMS Sequence, Refer to Appendix D.

4.5 DFTPP Ion Abundance Criteria, Refer to Appendix E.

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4.6 Quantitation Ions for All Target Analytes, Refer to Appendix F.

4.7 Acquisition Method/Operating Conditions, Refer to Appendix G.

4.8 MDL/RL and Control Limits Required Compounds, Refer to Appendix H.

5.0 EQUIPMENT & SUPPLIES:

5.1 Gas Chromatograph - An HP 6890 or equivalent analytical system complete with a temperature programmable gas chromatograph suitable for split or splitless injection and all required accessories including syringes, analytical columns, autosampler and gases.

5.2 GC Column - 30 m x 0.25 mm ID x 0.50μm film thickness bonded-phase silicone coated fused silica capillary column (Zebron ZB-5). A 1.0 μm film thickness or a 0.32 mm ID column may be desirable to increase chromatographic loading capacity for problem samples. A film thickness of 0.25 μm may also be used.

5.3 Mass Spectrometer – An HP 5973 Series Mass Selective Detector or equivalent capable of scanning from 35 to 500 AMU every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all required criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

5.4 Data System – The HP ChemStation computer system is interfaced to the mass spectrometer allowing the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The software allows for the searching of any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). The software also allows integrating the abundance of any EICP between specified time and scan number limits.

6.0 REAGENTS & STANDARDS:

6.1 Stock standard solutions - Standard solutions can be prepared from pure standard materials or purchased as certified solutions. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source. Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions as per suppliers' suggestions in bottles with Teflon-liners. Working standards are prepared in amber-glass GC

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vials with aluminum crimp top caps and stored in a refrigerator. Fresh standards should be prepared every twelve months at a minimum. The internal standard may be stored at room temperature if no degradation is noted. If degradation does occur, a new internal standard will be prepared and stored in a refrigerator.

6.2 GC/MS tuning standard - A methylene chloride solution containing 50 ng/µL decafluorotriphenylphosphine (DFTPP). The solution should also contain 50ng/uL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance.

6.3 Internal standard - The recommended internal standard is 4,4-dibromooctafluorobiphenyl (D.B.O.B.) in methylene chloride. The internal standard should permit most components of interest in a chromatogram to have retention times of 0.80 to 1.20 relative to the internal standards. Other compounds may be used if this requirement is met. Prior to analysis, each 1 mL sample extract should be spiked with a 10 µL of the internal standard solution resulting in a concentration of 10 ug/mL in the extract.

6.4 Calibration standards – The acid forms of the analytes present in the stock solutions must be derivatized as an intermediate prior to creating the calibration standards. Instructions for doing so are as follows:

6.4.1 An intermediate is prepared containing all compounds of interest and surrogates at 50 µg/mL concentration in an autosampler vial with a volume of exactly 1 mL. The level of solution in this vial is precisely marked, then allowed to evaporate until approximately 500 µL remains. About 1.5 mL of diazomethane solution is added to the vial and is mixed for 1 minute, then allowed to stand for 30 minutes. A yellow color should persist in the solution and no bubbles should be generated. If the color does not persist, the diazald has been consumed and more must be added until the yellow color persists.

6.4.2 To remove the diazomethane/ether from the intermediate, the solution is evaporated down to approximately 500 µL, then methylene chloride is used to bring the solution up to the original 1 mL solution mark on the vial. The vial is then re-capped and the result is the esterfied forms of the target analytes at a 50 µg/mL concentration.

6.4.3 The calibration levels are prepared from the derivitized intermediate. Currently used concentration levels are 0.25, 0.5, 1.0 2.0, 5.0, 7.5, 10, and sometimes 15 µg/mL in methylene chloride. All calibration standards should contain the internal standard at a concentration of 10.0 µg/mL.

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6.5 Surrogate standards - The recommended surrogate standard is a solution of 2,4-dichlorophenylacetic acid (D.C.A.A.) in acetone. Each sample should be spiked with surrogate standard solution prior to the extraction, resulting in a final extract concentration of 5 μg/mL.

7.0 INTERFERENCES & PROCEDURAL LIMITATIONS:

7.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles (TICPs). All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

7.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source.

8.0 SAMPLE ACCEPTANCE & HOLDING TIMES:

8.1 The samples must be protected from light and refrigerated at 4° C (±2° C) from the time of receipt until the extraction and analysis.

8.2 Extraction of water samples must be started within 7 days of sample collection and the extraction of soil/sediment samples must be started within 14 days.

8.3 Extracts of either water or soil/sediment samples must be analyzed within 40 days from extraction.

9.0 CALIBRATION & STANDARDIZATION:

9.1 Each GC/MS system must be hardware tuned to meet the criteria listed in Appendix E for a 50ng injection of decafluorotriphenylphosphine (DFTPP) every 12 hours. No sample analyses can begin until all these criteria are met.

9.2 The GC/MS tuning standard is also used to assess the GC column performance and injection port inertness. The degradation of DDT to DDE and DDD should not exceed 20%, and the response and peak shape of pentachlorophenol and benzidine are to be assessed to determine if injection port and/or column maintenance is required.

9.3 The internal standard selected should permit most components of interest in a chromatogram to have retention times of 0.80 to 1.20 relative to the internal standard. Use the most intense ion from the internal standard as the primary ion

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for quantification, i.e. for D.B.O.B use m/z 296 for quantification. If interferences are noted, use the next most intense ion as the quantitation ion. In order to quantitate by any ion other than the primary one, a calibration curve must be created using that ion. Quantitation ions for each target analyte, surrogate and internal standard are given in Appendix F.

9.4 A 10 ul aliquot of 1000 ug/mL internal standard solution is to be added to a 1.0 mL aliquot of calibration standards and sample extracts, resulting in a concentration of 10 ug/mL.

9.5 Analyze 1 μL of each calibration standard. Tabulate the retention times and areas of the primary characteristic ions against the standard level concentrations for each compound, including the surrogate compounds. A secondary ion may be used for quantitation if interferences with the primary ion are noted. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Calculate the relative response factors (RRF) for each compound, relative to the internal standard compound as follows:

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where: A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the relative internal standard
C_{is} = Concentration of the internal standard (μg/mL)
C_x = Concentration of the compound to be measured (μg/mL)

9.6 The average relative response factor (RRF) is to be calculated for all target compounds. The compounds are checked for a minimum average response factor of 0.050. As the reference standards or the components of the chromatographic system deteriorate, the average relative response factors tend to decrease.

9.7 If any of the target compounds do not meet the average minimum response factor criteria, the system must be evaluated and corrective action taken before any sample analysis begins.

9.8 Calculate the percent relative standard deviation (%RSD) for each calibrated compound using the relative response factors calculated at each of the various concentration levels using the following equation. Target analytes should have a maximum RSD of 30% for the calibration curve to be valid.

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$$\%RSD = \frac{SD}{RRF_{mean}} X100$$

Where: SD = standard deviation of the RRFs for a compound
RRF_{mean} = mean of the RRFs for a compound

9.9 If the %RSD of any reported compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

9.10 If the %RSD of any compounds is greater than 15%, construct calibration curves of area ratio (A_x/ A_{is}) versus concentration ratio (C_x/ C_{is}) using first or higher order regression fit of the calibration points. The analyst should select the regression order that introduces the least calibration error into the quantitation (i.e. coefficient of determination, (r) > 0.99). Six or more calibration levels are required for use of a quadratic curve. The use of calibration curves is a recommended alternative to average response factor calibration, and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system.

9.11 If the %RSD of any analyte of interest is greater than 30%, the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column and reanalyze the calibration standards.

9.12 The calibration must be checked against a second source standard. The second source standard may be the initial calibration verification or continuing calibration verification. The acceptance limits for the second source compounds are 80 to 120%.

9.13 A system performance check of the calibration curve must be performed once every 12 hours during analysis, using a mid-point calibration standard. The percent drift of each reported target compound must be checked. The percent drift is calculated for each reported target analyte using the equation below. If the percent difference for each reported analyte is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (>20% drift) for any reported analyte of interest, corrective action must be taken. If no source of the problem can be determined, a new calibration curve must be generated.

$$\%Drift = \frac{C_1 - C_c}{C_1} X100$$

Where: C_1 = Calibration check compound standard concentration
Cc = Measured concentration using selected quantitation method

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9.13.1 Internal standard responses and retention times in all standards must be evaluated. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each standard. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%) from the areas noted during the initial calibration, the mass spectrometric system must be inspected for malfunction and corrections made if appropriate. When the corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

10.0 PROCEDURE:

10.1 Sample Extract Preparation:

10.1.1 Sample extracts are prepared by approved methods. Each extract is concentrated to a final volume of 1.0 mL; if it cannot be concentrated down to 1.0 mL the data is qualified in LIMS.

10.1.2 Internal standard solution is added to each sample extract. For water and/or soil extracts, add 10 µL of internal standard solution to the accurately measured 1.0 mL of sample extract. Analyze the 1.0 mL extract by GC/MS using a bonded-phase fused silica capillary column.

10.1.3 NOTE: Any extract dilution indicated by sample characterization should be performed after the addition of internal standard. If any further dilutions of the extract are made, additional internal standard must be added to maintain the required 10 µL/mL of each constituent in the extract volume. If the concentration of any compound exceeds the initial calibration range, the extract must be diluted and reanalyzed. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitiation is performed, document the reasons in the QC Checklist in the data packet and submit a Track-It work order to the QA group.

10.1.4 Sample extracts with considerable sediment may be filtered through a 0.45 µm Whatman polysulfone filter after the addition of internal standard.

10.2 GC/MS Analysis:

10.2.1 The following instrumental parameters are required for all performance tests and for all sample analyses:

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Electron: 70 volts (nominal)
Mass Range: 35 to 500 amu
Scan Time: at least 1 scan per second

10.2.2 The GC acquisition method contains the operating conditions for analysis. Refer to Appendix G for suggested operating conditions.

10.3 Target Analyte Identification.

10.3.1 The compounds listed in the Target Compound List (TCL), Appendix F, shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

10.3.2 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within +/-0.06 RRT units of the RRT of the standard component. For reference, the standard must be run in the same 12-hour period as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

10.3.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the laboratory's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the laboratory's GC/MS meets the DFTPP daily tuning requirements. These standard spectra may be obtained from the run used to obtain reference RRTs.

10.3.4 The requirements for qualitative verification by comparison of mass spectra are as follows:

10.3.4.1 Ions present in the standard mass spectra at a relative intensity greater the 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

10.3.4.2 Relative intensities of ions specified in (1) should agree within plus or minus 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard

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spectra, the corresponding sample ion abundance must be between 20 and 80 percent.)

10.3.4.3 If a compound cannot be verified by all of the above criteria, but in the technical judgment of the mass spectral interpretation analyst the identification is correct, then the laboratory shall report that identification.

10.4 Tentatively Identified Compounds. A library search may be executed for non-TCL sample components for the purpose of tentative identification. For this purpose the NIST Mass Spectral Library shall be used. Guidelines for making tentative identification are as follows:

10.4.1 Up to 20 non-surrogate organic compounds of greatest apparent concentration not listed in Appendix F shall be tentatively identified via a forward search of the NIST mass spectral library.

10.4.2 Substances with responses less that 10% of the nearest internal standard are not required to be searched in the fashion.

10.4.3 Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation analyst assign a tentative identification.

10.4.4 The 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.

10.4.5 The relative intensities of the major ions should agree with ±20%. (Example: For an ion with an abundance of 50% in the standard spectra the corresponding sample ion abundance must be between 30 and 70 percent.

10.4.6 Molecular ions present in reference spectrum should be present in sample spectrum.

10.4.7 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.

10.4.8 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 compounds.

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10.4.9 If in the technical judgment of the mass spectral interpretation analyst, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral analyst should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

11.0 CALCULATIONS

11.1 TCL components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte. The EICP area of characteristic ions of analytes listed in Appendix F are used. Note: The continuing calibration internal response must fall within a factor of two (50 –200%) of the initial calibration mid-level standard response.

11.2 When 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 mean relative response factor (RRF_{mean}) or calibration curve from the initial calibration is used to calculate the concentration in the sample extract. Secondary ions may be used if interferences are present, which would adversely effect the calculated concentration. However, the area of a secondary ion cannot be substituted for the area of a primary ion unless a relative response factor or calibration curve is calculated using the secondary ion. If the %RSD of a compound's relative response factors was less than 15%, the extract concentration may be calculated using the RRF_{mean} from the initial calibration.

11.2.1 Calculate the concentration in the sample extract following the equation below. Alternatively, the regression line fitted to the initial calibration may be used for determination of the extract concentration.

$$C_{ext} = \frac{(A_x)(C_{is})}{(A_{is})(RRF_{mean})}$$

Where: C_{ext} = Concentration of the compound in extract (µg/mL)
A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the internal standard
C_{is} = Concentration of the internal standard in the extract (20 µg/mL)

11.2.2 The corresponding sample concentration is then calculated using the following equations:
Liquid samples

$$\mu g/L = (C_{ext})(V_{ext})(D)$$

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(V_o)

Where: V_{ext} = Extract volume (mL)
V_o = Sample volume extracted (L)
D = Extract dilution factor

Solid Samples

$$\mu g/g = mg/Kg = \frac{(C_{ext})(V_{ext})(D)}{(W_o)}$$

Where: V_{ext} = Extract volume (mL)
W_o = Sample weight extracted (g)
D = Extract dilution factor

11.3 Estimated concentrations for tentatively identified compounds are made using the equations given above, with the following modification: The areas A_x and A_{is} should be from the total ion chromatograms, and RRF for the compound should be assumed to be 1. Use the nearest internal standard free of interferences. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

11.4 Accuracy:

$$\% \text{ Matrix Spike Recovery} = \frac{SSR - SR}{SA} X\,100$$

SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

11.5 Precision - Relative Percent Difference

$$\% \text{ RPD} = \frac{|A - B|}{[(A + B)/2]} X\,100$$

Where A = Sample A Result
B = Sample B Result

12.0 DATA REDUCTION AND RECORDS

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12.1 Daily calibration checks are calculated against the most recent initial calibration. The calibration method used for quantitation is stated in the header information of the "Continuing Calibration Report", the processed data "Quantitation Report", and the instrument log.

12.2 A LIMS bench sheet is printed out which documents the sample preparation. Refer to Appendix A.

12.3 If there are non-conformances, these should be documented on the QC Checklist in the data packet and submitted as a Track-IT! work order which is forwarded to the QA group.

12.4 A data packet is created and the data is electronically transferred to the LIMS.

12.5 The data packet is submitted to a technical peer for review/validation, and the data becomes reportable after it is approved in the LIMS. This validation is documented.

12.6 The data packet is filed in the central archives in alphanumeric order by the sequence number generated by the LIMS. Data is kept for 10 years

13 REPORTING:

13.1 A report is generated by the laboratory Project Manager when all requested analyses have been completed and approved.

13.2 All sample data is reported to two significant figures; QC recoveries are reported to three significant figures.

14 QUALITY CONTROL:

14.1 A Continuing Calibration Check (CCV) is analyzed with each 12-hour clock. Refer to section 9.13. Percent difference of less than or equal to 20% is the acceptance criteria.

14.2 A method blank (MB), a laboratory control spike (LCS), a laboratory control spike duplicate (LCSD), a matrix Spike (MS) (when available) and a matrix spike duplicate (MSD) (when available) are analyzed with each sample preparation batch.

14.3 Calculate surrogate and spike standard recovery on all samples, blanks and matrix spikes. Determine if recovery is within limits.

14.4 Refer to Appendix H for control limit guidelines.

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14.5 If a MB, LCS, or LCSD is outside of the control limits, re-extract the batch of samples if possible. If this is not possible, qualify the samples associated with the batch QC that is outside acceptance limits.

14.6 If the MS/MSD is outside of the control limits and the LCS/LCSD is within control limits, qualify the samples on the project that was spiked.

14.7 If the surrogate is out of specification, corrective action must be taken. The sample may be reanalyzed. If the surrogate is still outside acceptance limits, re-extract the sample if more is available. If the re-extracted result is out of specification, qualify the data on that sample.

15 METHOD PERFORMANCE:

15.1 Precision and accuracy charts are used to determine if laboratory procedures are in or out of control and to identify developing trends of positive or negative bias.

16 DETECTION LIMITS:

16.1 Refer to Appendix H.

16.2 A reporting limit verification sample must be analyzed after each initial calibration, or monthly at a minimum (it can be a point on the calibration curve), at or below the reporting limit. Results must fall within +/- 40% of the true value. If results are not within the +/- 40% range, the reporting limit may be raised to the next standard that does pass acceptance limits or the calibration is not acceptable and corrective actions must be taken.

17.0 REFERENCES:

17.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods, EPA SW846, 3rd Edition, Integrated Manual, 8270C, Revision 3, December, 1996.

18.0 MANAGEMENT & POLLUTION PREVENTION:

18.1 Please refer to the general policies and procedures outlined in Chapter 7 of the QAM regarding waste management and pollution prevention.

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APPENDIX A:

LIMS Bench Sheet

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PREPARATION BENCH SHEET

B8K0085

Braun Intertec Corporation

Analysis: LIST 2 SOILS

Logbook:

Matrix: Soil

Analyst: RSS

Printed: 3/3/2009 2:44:40PM

Prepared using: ENVSVOCGCMS - EPA 3545

Surrogate ID: 8H13009

Lab Number	Prepared	Initial (g)	Final (mL)	Spike ID	uL Spike	Source ID	uL Surrogate	Position	Extraction Comments
0806615-01	11/05/08 11:10	30.31	1				50		
B8K0085-BLK1	11/05/08 11:10	30.09	1				50		
B8K0085-BS1	11/05/08 11:10	30.47	1	8B25013	50		50		
B8K0085-BSD1	11/05/08 11:10	30.04	1	8B25013	50		50		
B8K0085-MS1	11/05/08 11:10	30.36	1	8B25013	50	0806615-01	50		
B8K0085-MSD1	11/05/08 11:10	30.32	1	8B25013	50	0806615-01	50		

Reagent	Description
8B25013	MDA L2 spike std. 100UG/ML
8E16023	Acidified Sodium Sulfate
8F12063	Acetic Acid, Glacial
8H13009	MDA L2 Surrogate std. (DCAA)
8H22033	Ottawa Sand
8I11021	NaCl
8I29042	Acetone Pesticide Grade
8J06018	12 N H2SO4
8J06026	6N NaOH
8J17017	Diazomethane
8J24001	Methylene Chloride

APPENDIX B:

LIMS Standard Record

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Analytical Standard Record

Braun Intertec Corporation

8L03026

Description:	MDA L2 Surrogate std. (DCAA)	Expires:	06/01/09
Standard Type:	Surrogate Spike	Prepared:	12/03/08
Solvent:	Acetone trace 6E05017	Prepared By:	Rupali Sawant
Final Volume (mls):	10	Department:	ENVSVOCGCMS
Vials:	1	Last Edit:	12/03/08 14:27 by RSS

MDA List 2 Surrogate Stock (2,4-Dichlorophenylacetic acid) 6G06018, 500ul diluted to 10ml with acetone

Analyte	CAS Number	Concentration	Units
D.C.A.A.	19719-28-9	100	ug/mL

Parent Standards used in this standard:

Standard	Description	Prepared	Prepared By	Expires	Last Edit	(mls)
7F06021	MDA LIST2 SURROGATE STOC	06/06/07	Jamie Ryan	04/01/09	07/11/07 11:09 by JLR	0.5

Reviewed By Date

APPENDIX C:

GC/MS SVOC Run Log

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BRAUN
INTERTEC

Date: __________ Analyst: __________ Run ID: ______________ I/S ID: ______________ Amount (μL): __________

SOP: ______________________________ ICAL Run ID: ____________ Tune ID: ____________________________

ICAL File: C:\MSD\1\METHODS____

Tune File: C:\MSD\1____

Data File: D:\MSD\1\DATA____

Column ID: ______________________ Injection Port __________ Seal __________ Septa _________ Liner _________

Other (Refer to Appropriate Major Maintenance Logbook as Necessary):

Seq. #	Sample ID	Traceability ID	Dilution	Comments

RUN ID: _______________ (Continued)

Seq. #	Sample ID	Traceability ID	Dilution	Comments

APPENDIX D:

LIMS Sequence

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ANALYSIS SEQUENCE

8K13004

Analysis:

Instrument: GCMS-C

Calibnration ID: UNASSIGNED

Analyst:

Logbook:

Printed: 3/3/2009 3:02:35PM

Lab Number	Analysis	Dilution	Position	STD ID	ISTD ID	Comments
8K13004-TUN1	QC			8G11035		
8K13004-CAL1	QC			8C19013		
8K13004-LCV1	QC			8C19013		
8K13004-CAL2	QC			8C19014		
8K13004-LCV2	QC			8C19014		
8K13004-CAL3	QC			8C19015		
8K13004-LCV3	QC			8C19015		
8K13004-CAL4	QC			8C19016		
8K13004-CAL5	QC			8C19017		
8K13004-CAL6	QC			8C19018		
8K13004-CAL7	QC			8C19019		
8K13004-CAL8	QC			8C19020		
8K13004-SCV1	QC			7L20018		
8K13004-CCV1	QC			8C19018		
B8K0085-BLK1	QC				8H14018	
B8K0085-BS1	QC				8H14018	
B8K0085-BSD1	QC				8H14018	
B8K0085-MS1	QC				8H14018	
B8K0085-MSD1	QC				8H14018	
0806615-01	Sample				8H14018	

UMP006734

APPENDIX E:

DFTPP Ion Abundance Criteria

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DFTPP Ion Abundance Criteria

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

APPENDIX F

Quantation Ions for All Analytes

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UMP006737

Characteristic Ions for MDA1 Compounds

Parameter	Quantitation Ion	Identification Ions
D.B.O.B.	456	296,454,458
3,5-D.C.B.A	173	204,175
D.C.A.A	159	183,218
Dicamba	203	205,234
Mercoprop	142	169,228
M.C.P.A.	214	155,141
Dichlorprop	162	189,148
2,4-D	199	234,175
Trichlopyr	212	210,268
Pentachlorophenol	280	265,237
2,4,5-TP (Silvex)	196	235,283
Chloramben	219	188,190,221
2,4,5-T	233	268,270
Dinoseb	225	254,195
2,4-DB	101	59,162
Bentazon	212	105,254
Picloram	196	198,254,223
D.C.P.A	301	299,332,330

All analytes are also compared to full reference spectra for identification.

APPENDIX G

Acquisition Method/Operating Conditions

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UMP006739

TOPLEVEL PARAMETERS

```
Method Information For: C:\MSDCHEM\1\METHODS\2008MDAL2.M
Method Sections To Run:

   ( ) Save Copy of Method With Data
   ( ) MSTOP                 Pre-Run Cmd/Macro  =
   ( ) Instrument Control Pre-Run Cmd/Macro  =
   ( ) Data Analysis         Pre-Run Cmd/Macro  =
   (X) Data Acquisition
   (X) Data Analysis
   ( ) MSTOP                 Post-Run Cmd/Macro =
   ( ) Instrument Control Post-Run Cmd/Macro =
   ( ) Data Analysis         Post-Run Cmd/Macro =
Method Comments:
  This is the default method
```

END OF TOPLEVEL PARAMETERS

INSTRUMENT CONTROL PARAMETERS

6890 GC METHOD

```
OVEN
   Initial temp:  55 'C (On)                Maximum temp:  360 'C
   Initial time:  1.00 min                  Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp  Final time
      1 30.00      175        0.00
      2  7.50      220        0.00
      3 30.00      350        2.50
      4   0.0(Off)
   Post temp:  0 'C
   Post time:  0.00 min
   Run time:  17.83 min

FRONT INLET (SPLIT/SPLITLESS)            BACK INLET (UNKNOWN)
   Mode:  Pulsed Splitless
   Initial temp:  275 'C (On)
   Pressure:  13.13 psi (On)
   Pulse pressure:  40.0 psi
   Pulse time:  1.00 min
   Purge flow:  50.0 mL/min
   Purge time:  1.00 min
   Total flow:  53.4 mL/min
   Gas saver:  On
   Saver flow:  15.0 mL/min
   Saver time:  2.00 min
   Gas type:  Helium

COLUMN 1                                 COLUMN 2
   Capillary Column                         (not installed)
   Model Number:  Zebro ZB-5
   5% Phenyl
   Max temperature:  360 'C
   Nominal length:  30.0 m
   Nominal diameter:  250.00 um
```


UMP006740

```
    Nominal film thickness:  0.50 um
    Mode:  constant flow
    Initial flow:  1.5 mL/min
    Nominal init pressure:  13.14 psi
    Average velocity:  45 cm/sec
    Inlet:  Front Inlet
    Outlet:  MSD
    Outlet pressure:  vacuum
```

```
 FRONT DETECTOR (NO DET)

 SIGNAL 1
    Data rate:  20 Hz
    Type:  test plot
    Save Data:  Off
    Zero:  0.0 (Off)
    Range:  0
    Fast Peaks:  Off
    Attenuation:  0

 COLUMN COMP 1
    (No Detectors Installed)
```

```
 BACK DETECTOR (NO DET)

 SIGNAL 2
    Data rate:  20 Hz
    Type:  test plot
    Save Data:  Off
    Zero:  0.0 (Off)
    Range:  0
    Fast Peaks:  Off
    Attenuation:  0

 COLUMN COMP 2
    (No Detectors Installed)
```

```
 THERMAL AUX 2
    Use:  MSD Transfer Line Heater
    Description:
    Initial temp:  315 'C (On)
    Initial time:  0.00 min
       #  Rate  Final temp  Final time
       1   0.0(Off)
```

```
 POST RUN
    Post Time: 0.00 min
```

```
 TIME TABLE
    Time       Specifier                    Parameter & Setpoint
```

7673 Injector

```
      Front Injector:
         Sample Washes                0
         Sample Pumps                 4
         Injection Volume           1.0 microliters
         Syringe Size              10.0 microliters
         Nanoliter Adapter          Off
         PostInj Solvent A Washes     4
         PostInj Solvent B Washes     4
         Viscosity Delay              2 seconds
         Plunger Speed             Fast
         PreInjection Dwell        0.00 minutes
         PostInjection Dwell       0.02 minutes

      Back Injector:
No parameters specified

 Column 1 Inventory Number :
 Column 2 Inventory Number :
```

MS ACQUISITION PARAMETERS

```
General Information
------- -----------

Tune File                  : TUN9007.U
Acquistion Mode            : Scan
```

MS Information
-- -----------

```
Solvent Delay            : 2.85 min

EM Absolute              : False
EM Offset                : 0
Resulting EM Voltage     : 1305.9

[Scan Parameters]

Low Mass                 : 35.0
High Mass                : 500.0
Threshold                : 25
Sample #                 : 2        A/D Samples    4

[MSZones]

MS Quad                  : 150 C    maximum 200 C
MS Source                : 230 C    maximum 250 C
```

END OF MS ACQUISITION PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

DATA ANALYSIS PARAMETERS

Method Name: C:\MSDCHEM\1\METHODS\2008MDAL2.M

Percent Report Settings

Sort By: Signal

Output Destination
    Screen: No
    Printer: Yes
    File: No

Integration Events: Meth Default

Generate Report During Run Method: No

Signal Correlation Window: 0.020

Qualitative Report Settings

Peak Location of Unknown: Apex

Library to Search   Minimum Quality
C:\DATABASE\NBS75K.L   0

Integration Events: Meth Default

Report Type: Summary

Output Destination
    Screen: No
    Printer: Yes
    File: No

Generate Report During Run Method: No

Quantitative Report Settings

Report Type: Summary

Output Destination
    Screen: Yes
    Printer: No
    File: No

Generate Report During Run Method: No

MDA1 acqusition method
Calibration Last Updated:

Reference Window: 2.00 Minutes
Non-Reference Window: 1.00 Minutes
Correlation Window: 0.10 minutes
Default Multiplier: 1.00
Default Sample Concentration: 0.00

Compound Information

*** Empty Quantitation Database ***

END OF DATA ANALYSIS PARAMETERS

Thu Feb 19 08:19:23 2009

Additional Information for BMDAL1.M
File created Mon Apr 11 17:02:00 2005

Method : C:\MSDCHEM\1\METHODS\BMDAL1.M
Renamed: C:\MSDCHEM\1\METHODS\BMDAL2.M
Mon Apr 11 17:02:46 2005

Method : C:\MSDCHEM\1\METHODS\BMDAL2.M
Renamed: C:\MSDCHEM\1\METHODS\MDALIST2.M
Tue Apr 19 13:08:46 2005

Method : C:\MSDCHEM\1\METHODS\BMDALIST2.M
Renamed: C:\MSDCHEM\1\METHODS\MDALIST2.M
Wed Oct 12 07:41:21 2005

Method : C:\MSDCHEM\1\METHODS\MDALIST2.M
Renamed: C:\MSDCHEM\1\METHODS\2008MDAL2.M
Thu Oct 09 14:17:05 2008

APPENDIX H

MDL/RL and Control Limits

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Braun Intertec Corporation

Analytical Method Information

8270 MDA LIST 2 SOILS in Soil (EPA 8270C)

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Dicamba	0.0080	0.050 mg/kg		30	30 - 110	25	50 - 115	25
M.C.P.A.	0.014	0.050 mg/kg		30	30 - 120	25	45 - 110	25
2,4-D	0.012	0.050 mg/kg		30	30 - 120	25	50 - 115	25
Triclopyr	0.0060	0.050 mg/kg		30	40 - 120	25	80 - 120	25
Pentachlorophenol	0.0070	0.050 mg/kg		30	40 - 125	25	40 - 130	25
2,4,5-T.P.	0.0070	0.050 mg/kg		30	40 - 130	25	60 - 120	25
2,4,5-T	0.0090	0.050 mg/kg		30	30 - 130	25	50 - 115	25
Dinoseb	0.0050	0.050 mg/kg		30	30 - 120	25	30 - 120	25
2,4-D.B.	0.011	0.050 mg/kg		30	55 - 125	25	70 - 120	25
Bentazon	0.0090	0.050 mg/kg		30	40 - 120	25	55 - 120	25
Picloram	0.011	0.050 mg/kg		30	30 - 140	25	60 - 100	25
surr: D.C.A.A.			45 - 125					
D.B.O.B.								

Braun Intertec Corporation

Analytical Method Information

8270 MDA LIST 2 WATERS in Water (EPA 8270C)

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Dicamba	0.38	0.50 ug/L		25	75 - 140	25	80 - 130	20
M.C.P.A.	0.29	0.30 ug/L		25	60 - 140	25	80 - 130	20
2,4-D	0.26	0.50 ug/L		25	75 - 140	25	80 - 135	20
Triclopyr	0.41	0.50 ug/L		25	75 - 125	25	80 - 125	20
Pentachlorophenol	0.39	0.50 ug/L		25	70 - 125	25	80 - 125	20
2,4,5-T.P.	0.28	0.50 ug/L		25	80 - 135	25	80 - 135	20
2,4,5-T	0.31	0.50 ug/L		25	70 - 140	25	70 - 140	20
Dinoseb	0.34	0.50 ug/L		25	70 - 130	25	75 - 125	20
2,4-D.B.	0.15	0.50 ug/L		25	80 - 140	25	80 - 140	20
Bentazon	0.22	0.50 ug/L		25	70 - 140	25	80 - 140	20
Picloram	0.25	0.50 ug/L		25	45 - 140	25	60 - 125	20
surr: D.C.A.A.			70 - 130					
D.B.O.B.								

DESCRIPTION:

The Determination of MN Department of Agriculture List 1 (MDA1) Organo-Phosphorus, Organo-Chlorine, Nitrogen-containing and Triazine Pesticides in Aqueous and Solid Samples by Gas Chromatography/Mass Spectrometry (GC/MS).

SUMMARY:

Prior to analysis, samples should be prepared using an appropriate sample preparation method. Water samples are prepared according to EPA Method 3520C. Soil samples are prepared according to EPA Method 3545. This SOP is applicable to the analysis of all liquid and solid matrices for List 1 compounds. Qualitative identification of the components in the extract is performed by comparison of the retention time and mass spectra to that of a reference standard. Quantitative analysis is performed using integrated area abundance of the extracted ion current profile (EICP) of the primary characteristic ion for each target analyte, relative to that of an internal standard.

SCOPE:

This procedure is based on the US EPA SW-846 Method 8270C for extractable semivolatile organic compounds by GC/MS. This method is used to determine the concentration of semivolatile organic compounds that are amenable to GC/MS in extracts prepared from all types of solid waste matrices, soils and ground water. The Minnesota Department of Agriculture List 1 (MDA1) is routinely analyzed. This procedure complies with the requirements of the Resource Conservation and Recovery Act (RCRA) and the Minnesota Department of Agriculture Incident Response Program. This SOP applies to the analysis portion only. Please refer to the MDA1SOILPREP and MDA1H2OPREP SOPs for the sample preparation procedures.

DOCUMENT CONTINUITY:

This document replaces Braun Intertec Corporation SOP GCMS8270MDAL1 Revision 2.

SIGNATURES:

Quality Assurance ______________ **Date** 3/4/09
Michelle Hubanks

Technical Lead ______________ **Date** 3/3/09
Mike Frencl

Laboratory Manager ______________ **Date** 03/03/09
Thomas P. Wagner

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1.0 PERSONNEL QUALIFICATIONS:

1.1 Personnel performing this procedure must be qualified per the requirements outlined in chapter 1 of the Analytical Laboratory Quality Assurance Manual (QAM).

2.0 SAFETY:

2.1 Personnel performing this procedure must follow general laboratory safety practices as defined in chapter 1 of the (QAM).

2.2 Review all Material Safety Data Sheets (MSDS) for chemicals used in this procedure.

2.3 Wear solvent-resistant gloves when working with samples, extracts, and solvents.

2.4 Work under a fume hood when extracting samples, preparing dilutions, or making standards.

3.0 DEFINITIONS:

3.1 Refer to standardized Braun Intertec Corporation definitions as described in chapter 4 of the QAM.

3.2 $MeCl_2$: Methylene Chloride.

3.3 LIMS: Laboratory Information Management System.

3.4 Element: The LIMS used by the Analytical Laboratory.

4.0 FORMS & RECORDS:

4.1 LIMS Bench Sheet, Refer to Appendix A.

4.2 LIMS Standard Record, Refer to Appendix B.

4.3 GC/MS SVOC Run Log, Form ORG 24, Refer to Appendix C.

4.4 LIMS Sequence Sheet, Refer to Appendix D.

4.5 DFTPP Ion Abundance Criteria, Refer to Appendix E.

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4.6 Quantitation Ions for Target Analytes, Refer to Appendix F.

4.7 Acquisition Method/Operating Conditions, Refer to Appendix G.

4.8 MDL/RL and Control Limits for compounds, Refer to Appendix H.

5.0 EQUIPMENT & SUPPLIES:

5.1 Gas Chromatograph - An HP 6890 or equivalent analytical system complete with a temperature programmable gas chromatograph suitable for split or splitless injection and all required accessories including syringes, analytical columns, autosampler and gases.

5.2 GC Column - 30 m x 0.25 mm ID x 0.50 µm film thickness bonded-phase silicone coated fused silica capillary column (Zebron ZB-5) or equivalent. A 1.0 µm film thickness or a 0.32 mm ID column may be desirable to increase chromatographic loading capacity for problem samples. A film thickness of 0.25 µm may also be used.

5.3 Mass Spectrometer – An HP 5973 or equivalent Series Mass Selective Detector capable of scanning from 35 to 500 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all required criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

5.4 Data System - The HP ChemStation computer system is interfaced to the mass spectrometer allowing the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The software allows for the searching of any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). The software also allows integrating the abundance of any EICP between specified time and scan number limits.

6.0 REAGENTS & STANDARDS:

6.1 Stock standard solutions – Standard solutions can be prepared from pure standard materials or purchased as certified solutions. When the compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used if they are certified by the manufacturer or by an independent source. Great care must be taken to maintain the integrity of all

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UMP006750

standard solutions. Store all standard solutions as per suppliers instructions in bottles with Teflon®-liners. Working standards are prepared in amber-glass GC vials with aluminum crimp top caps and stored in a refrigerator. Fresh standards should be prepared every twelve months at a minimum. The internal standard solution may be stored at room temperature if no degradation is noted. This prevents the Trifluralin-d_{14} from crystallizing out of solution. If degradation is noted a new standard will be prepared and stored in a refrigerator.

6.2 Calibration Standards - Prepare calibration standards at a minimum of five concentration levels. Each calibration standard should contain each compound of interest and each surrogate standard. The currently used concentration levels are 0.2, 0.5, 1.0, 2.0, 5.0, 10, 15, and 20 ug/mL. All calibration standards must contain the internal standard at a constant concentration of 5.0 ug/mL. Sonicate and mix stock standard well before making intermediate calibration standard and spike solution as simazine has a tendency to precipitate out of solution at higher concentrations (~>250 ug/mL).

6.3 GC/MS tuning standard - A methylene chloride solution containing 50 ug/mL of decafluorotriphenylphosphine (DFTPP). The solution should also contain 50 ug/mL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance.

6.4 Internal standard - The internal standard is Trifluralin-d_{14}. Each 1.0 mL sample extract should be spiked with 10 uL of the internal standard solution.

6.5 Surrogate standards - The recommended surrogate standard is an acetone solution containing Atrazine-d_5 and Diazinon-d_{10}. Each sample should be spiked with 100 uL of the solution prior to extraction, resulting in a final concentration of 10ug/mL. Newly prepared surrogate spiking standard should be verified prior to use in the samples.

7.0 INTERFERENCES & PROCEDURAL LIMITATIONS:

7.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles (TICPs). All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

7.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source.

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8.0 SAMPLE ACCEPTANCE & HOLDING TIMES:

8.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until extraction and analysis.

8.2 Extraction of water samples must be started within 7 days of sample collection and the extraction of soil/sediment samples must be started within 14 days.

8.3 Extracts of either water or soil/sediment samples must be analyzed within 40 days from extraction.

9.0 CALIBRATION & STANDARDIZATION:

9.1 Each GC/MS system must be hardware tuned to meet the criteria listed in Appendix E for a 50 ng injection of decafluorotriphenylphosphine (DFTPP) every 12 hours. No sample analyses can begin until all these criteria are met.

9.2 The GC/MS tuning standard is used to assess the GC column performance and injection port inertness every 12 hours. The degradation of DDT to DDE and DDD, and the response and peak shape of pentachlorophenol and benzidine are to be assessed to determine if injection port and/or column maintenance is required.

9.3 The internal standard selected should permit most components of interest in a chromatogram to have retention times of 0.80 to 1.20 relative to the internal standard. Use the base peak ion from the internal standard as the primary ion for quantification, i.e. for Trifluralin-d_{14} use m/z 315 for quantification. If interferences are noted, use the next most intense ion as the quantitation ion. Quantitation ions for each target analyte, surrogate and internal standard are given in Appendix F. A calibration curve composed of a given quant ion must be made before samples are allowed to be quantitated via that same quant ion.

9.4 A 10 µL aliquot of 500 µg/mL internal standard solution is to be added to a 1.0 mL aliquot of calibration standards and sample extracts, resulting in a concentration of 5.0 µg/mL.

9.5 Analyze 1 µL of each calibration standard. Tabulate the retention times and the areas of the primary characteristic ions against the standard level concentrations for each compound, including the surrogate compounds. A secondary ion may be used for quantitation if interferences with the primary ion are noted. Calculate Relative Response Factors (RRF) for each compound using the following equation:

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$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where: A_x = Area of the characteristic ion for the compound to be measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the internal standard (µg/mL).
C_x = Concentration of the compound to be measured (µg/mL).

9.6 The average relative response factor (RRF) is to be calculated for all target compounds. The compounds are checked for a minimum average relative response factor of 0.050. As the reference standards or the components of the chromatographic system deteriorate, the average relative response factors tend to decrease.

9.7 If any of the target compounds do not meet the minimum response factor, the system must be evaluated and corrective action taken before any sample analysis begins.

9.8 Calculate the percent relative standard deviation (%RSD) for each calibrated compound using the relative response factors calculated at each of the various concentration levels using the following equation. Target analytes should have a maximum RSD of 30% for the calibration curve to be valid.

$$\%RSD = \frac{SD}{RRF_{mean}} X100$$

Where, SD = standard deviation of the RRFs for a compound
RRF_{mean} = mean of the RRFs for a compound.

9.9 If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

9.10 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A_x/A_{is}) versus concentration ratio (C_x/C_{is}) using first or higher order regression fit of the calibration points. The analyst should select the regression order that introduces the least calibration error into the quantitation (i.e. coefficient of determination (r) > 0.99). Six or more calibration levels are required for use of a quadratic curve. The use of calibration curves is a recommended alternative to

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average response factor calibration, and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system.

9.11 The calibration must be checked against a second source standard. The second source standard may be the initial calibration verification or continuing calibration verification. The acceptance limits for the second source compounds are 80 to 120%.

9.12 A system performance check must be made before this calibration curve is used. A check of the calibration curve must be performed once every 12 hours during analysis, using a mid-point calibration standard. The percent drift of target compounds must be checked. The percent drift is calculated for each target analyte using:

$$\% Drift = \frac{C_1 - C_c}{C_1} \times 100$$

where: C_1 = Calibration check compound standard concentration.
C_c = Measured concentration using selected quantitation method.

If the percent difference for each target analyte is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% drift) for any analyte of interest, corrective action must be taken. If no source of the problem can be determined, a new calibration curve must be generated.

9.13 Internal standard responses and retention times in all standards must be evaluated. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each standard. If EICP area for any internal standard changes by more than a factor of two (-50% to +100%) from the areas noted during the initial calibration, the GC/MS system must be inspected for malfunction and corrections made if appropriate. Once corrections have been made and the system has been verified as working properly, reanalyze the samples that were analyzed while the system was malfunctioning.

10.0 PROCEDURE:

10.1 Sample Extract Preparation.

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10.1.1 Sample extracts are prepared by approved methods. Each extract is concentrated to a final volume of 1.0 ml.

10.1.2 Internal standard solution is added to each sample extract. For water and/or soil extracts, add 10 µL of internal standard solution to the accurately measured 1.0 mL of sample extract. Analyze the 1.0 mL extract by GC/MS using a bonded-phase fused silica capillary column.

10.1.3 ***Note:*** *Any extract dilution indicated by sample characterization should be performed after the addition of internal standards. If any further dilutions of the extracts are made, additional internal standard must be added to maintain the required 5 µg/mL of each constituent in the extract volume. If the concentration of any compound exceeds the initial calibration range, the extract must be diluted and reanalyzed. Secondary ion quantitation is* ***only*** *allowed when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reasons on the QC Checklist in the data packet and submit a Track-IT! Work order to the QA group.*

10.1.4 Sample extracts with considerable sediment may be filtered through a 0.45 µm Whatman polysulfone filter after the addition of internal standard.

10.2 GC/MS Analysis.

10.2.1 The following instrumental parameters are required for all performance tests and for all sample analyses.

Electron: 70 volts (nominal)
Mass Range: 35 to 500 amu
Scan Time: at least 1 scan per second

10.2.2 The GC acquisition method contains the operating conditions for analysis. Refer to Appendix G for suggested operating conditions.

10.3 Target Analyte Identification.

10.3.1 The compounds listed in the Target Compound List (TCL), Appendix F, shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2)

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correspondence of the sample component and standard component mass spectra.

10.3.2 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run in the same 12-hour period as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

10.3.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the laboratory's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, <u>only</u> if the laboratory's GC/MS meets the DFTPP daily tuning requirements. These standard spectra may be obtained from the run used to obtain reference RRTs.

10.3.4 The requirements for qualitative verification by comparison of mass spectra are as follows:

10.3.4.1 Ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

10.3.4.2 Relative intensities of ions specified in (1) should agree within plus or minus 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 20 and 80 percent.)

10.3.4.3 If a compound cannot be verified by all of the above criteria, but in the technical judgment of the mass spectral interpretation analyst, the identification is correct, then the laboratory shall report that identification.

10.4 Tentatively Identified Compounds. A library search may be executed for non-TCL sample components for the purpose of tentative identification. For this purpose the NIST Mass Spectral Library shall be used. Guidelines for making tentative identification are as follows:

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10.4.1 Up to 20 non-surrogate organic compounds of greatest apparent concentration not listed in Appendix F for the combined neutral extractable pesticides fraction shall be tentatively identified via a forward search of the NIST mass spectral library.

10.4.2 Substances with responses less than 10% of the nearest internal standard are not required to be searched in this fashion.

10.4.3 Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation analyst assign a tentative identification.

10.4.4 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.

10.4.5 The relative intensities of the major ions should agree within ±20%. Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance should be between 30 and 70 percent.

10.4.6 Molecular ions present in the reference spectrum should be present in the sample spectrum.

10.4.7 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.

10.4.8 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 compounds.

10.4.9 If in the technical judgment of the mass spectral interpretation analyst, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral analyst should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

11.0 CALCULATIONS:

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11.1 TCL components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte. The EICP area of characteristic ions of analytes listed in Appendix F are used. *Note: The continuing calibration internal standard response must fall within a factor of two (50 - 200 %) of the initial calibration mid-level standard response.*

11.2 When 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. If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average response factor (RRF) from the initial calibration data and the equation listed below. Secondary ions may be used if interferences are present. The area of a secondary ion cannot be substituted for the area of a primary ion unless a relative response factor is calculated using the secondary ion.

11.2.1 Calculate the concentration in the sample extract as follows:

$$C_{ex}(\mu g / mL) = \frac{(A_x \times C_{is})}{(A_{is} \times RRF)}$$

where C_{ex} is the concentration of the compound in the extract, and the other terms are as defined in Section 9.5. Alternatively, the regression line fitted to the initial calibration may be used for determination of the extract concentration.

11.2.2 Compute the concentration of the analyte in the sample using the following equations:

Liquids

The concentration of the analyte in the sample is calculated using the concentration of the analyte in the extract and the volume of the liquid sample extracted, as follows:

$$\mu g / L = \frac{(C_{ex} \times V_{ex})}{V_o} \times D$$

where:

V_{ex} = extract volume, in mL

V_o = volume of liquid extracted, in L.

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D = dilution factor

Solids
The concentration of the analyte in the sample is calculated using the concentration of the analyte in the extract and the weight of the solid sample extracted, as follows:

$$mg/kg = \frac{(C_{ex} \times V_{ex})}{W_s} \times D \times \frac{1}{1000}$$

where:

V_{ex} = extract volume, in mL
W_s = sample weight, in kg.
D = dilution factor

11.3 Estimated concentration for non-TCL components tentatively identified shall be quantified by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.3.1 The formula for calculating concentrations is the same as in section 11.2.1. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

11.4 Accuracy:

$$\%\,Matrix\ Spike\ Recovery = \frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

11.5 Precision: Relative Percent Difference

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$$RPD = \frac{|A - B|}{[(A + B)/2]} \times 100$$

Where: A = Sample A Result
B = Sample B Result

12.0 DATA REDUCTIONS & RECORDS:

12.1 Daily calibration checks are calculated against the most recent initial calibration. The calibration method used for quantitation is stated in the header information of the "Continuing Calibration Report", the processed data "Quantitation Report", and the instrument run log.

12.2 A LIMs bench sheet is printed out which documents the sample preparation. Refer to Appendix A.

12.3 If there are non-conformances, these should be documented on the QC Checklist in the data packet and submitted as a Track-IT! work order which is forwarded to the QA group.

12.4 A data packet is created and the data is electronically transferred to the LIMS.

12.5 The data packet is submitted to a technical peer for review/validation, and the data becomes reportable after it is approved in the LIMS. This validation is documented.

12.6 The data packet is filed in the central archives in alphanumeric order by the sequence number generated by the LIMS. Data is kept for 10 years.

13.0 REPORTING:

13.1 A report is generated by the laboratory project manager when all requested analyses have been completed and approved.

13.2 All data is reported to two significant figures.

14.0 QUALITY CONTROL:

14.1 A continuing calibration check (CCV) is analyzed with each 12-hour clock. Refer to section 9.11. Percent difference of $\leq$20% is the acceptance criteria.

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14.2 A method blank (MB), a laboratory control sample (LCS), a laboratory control sample duplicate (LCSD), a matrix spike (MS) (when available), and a matrix spike duplicate (MSD) (when available) are analyzed with each sample preparation batch.

14.3 Surrogates are spiked into each sample and QC checked.

14.4 Refer to Appendix H for control limit guidelines.

14.5 If a MB, LCS, or LCSD is outside of the control limits, re-extract the batch of samples, if possible. If this is not possible, qualify the samples associated with the out-of-specification batch QC.

14.6 If the MS/MSD is outside of the control limits and the LCS/LCSD is within the control limits, qualify the samples on the project that was spiked.

14.7 If a surrogate is out of specification, corrective action must be taken. The sample may be reanalyzed. If it is still out, re-extract the sample if more is available. If the re-extracted result is out of specification qualify the data on that sample.

15.0 METHOD PERFORMANCE:

15.1 Precision and accuracy charts are used to determine if laboratory procedures are in or out of control, and to identify developing trends of positive or negative bias.

16.0 DETECTION LIMITS:

16.1 Refer to Appendix H for a list of detection and reporting limits.

16.2 A reporting limit verification sample must be analyzed after each initial calibration, or monthly at a minimum, at or below the reporting limit. This result can be taken directly from the calibration curve. Results must fall within +/- 40 % the true value. If the results are not within +/- 40% the reporting limit may be raised to the next standard that does pass acceptance limits or the calibration is not acceptable.

17.0 REFERENCES:

17.1 PRIMARY REFERENCES:

17.1.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods, EPA SW846, 3rd Edition, Integrated Manual, 8270C, Revision 3, December, 1996.

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17.1.2 Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, 40 CFR, part 136, Appendix A, Method 625, 1994.

18 WASTE MANAGEMENT & POLLUTION PREVENTION:

18.1 Please refer to the general policies and procedures outlined in chapter 7 of the QCM regarding waste management and pollution prevention.

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Appendix A:

LIMS Bench Sheet

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UMP006763

PREPARATION BENCH SHEET

B9C0008

Braun Intertec Corporation

Analysis: List 1 Soil
Logbook:
Matrix: Soil

Analyst: RDS
Printed: 3/3/2009 3:18:16PM
Surrogate ID: 9A27011

Prepared using: ENVSVOCGCMS - EPA 3545

Lab Number	Prepared	Initial (g)	Final (mL)	Spike ID	uL Spike	Source ID	uL Surrogate	Position	Extraction Comments
0900817-05	03/02/09 08:59	30.15	1				100		
B9C0008-BLK1	03/02/09 08:59	30.1	1				100		
B9C0008-BS1	03/02/09 08:59	30.01	1	9B05040	500		100		
B9C0008-BSD1	03/02/09 08:59	30.02	1	9B05040	500		100		
B9C0008-MS1	03/02/09 08:59	30.15	1	9B05040	500	0900817-05	100		
B9C0008-MSD1	03/02/09 08:59	30.18	1	9B05040	500	0900817-05	100		

Reagent	Description
8K11005	Acetone Pesticide Grade
8L18055	Ottawa Sand
9A27011	MDA List 1 Surrogate 100 ug/mL
9A30005	Sodium Sulfate
9B05040	MDA L1 SPIKE SOLN, 20ug/ml
9B24021	Methylene Chloride

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Appendix B:

LIMS Standard Record

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UMP006765

Analytical Standard Record

Braun Intertec Corporation

9A27011

Description:	MDA List 1 Surrogate 100 ug/mL	Expires:	02/01/09
Standard Type:	Surrogate Spike	Prepared:	01/27/09
Solvent:	8K11005	Prepared By:	Robert D. Schmidt
Final Volume (mls):	5	Department:	ENVSVOCGCMS
Vials:	1	Last Edit:	01/27/09 08:22 by RDS

1 ml stock diluted to 5ml with acetone

Analyte	CAS Number	Concentration	Units
Diazinon-d10		100	ug/mL
Atrazine-d5		100	ug/mL

Parent Standards used in this standard:

Standard	Description	Prepared	Prepared By	Expires	Last Edit	(mls)
7G24005	MDA L1 Surrogate Stock (500ug/n	07/24/07	Jamie Ryan	02/01/09	07/24/07 11:27 by JLR	1

Reviewed By _______________ Date

UMR006766

Appendix C:

GC/MS SVOC Run Log

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Appendix D:

LIMS Sequence

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ANALYSIS SEQUENCE

8J28021

Analysis:

Instrument: GCMS-B

Calibnration ID: UNASSIGNED

Analyst:

Logbook:

Printed: 3/3/2009 3:17:59PM

Lab Number	Analysis	Dilution	Position	STD ID	ISTD ID	Comments
8J28021-TUN1	QC			8G11035		
8J28021-CCV1	QC			8D17014	5K02019	
B8J0570-BLK1	QC				8I29002	
B8J0570-BS1	QC				8I29002	
B8J0570-BSD1	QC				8I29002	
0806433-01	Sample				8I29002	
0806433-02	Sample				8I29002	
0806433-03	Sample				8I29002	
0806433-04	Sample				8I29002	
0806545-01	Sample				8I29002	Due 10/30/08 - Return sample to box. See CL.
0806545-02	Sample				8I29002	Due 10/30/08 - Return sample to box. See CL.
0806545-02RE1	Sample				8I29002	Re-extract added 10/29/2008 by NPL
0806545-03	Sample				8I29002	Due 10/30/08 - Return sample to box. See CL.
0806545-04	Sample				8I29002	Due 10/30/08 - Return sample to box. See CL.
0806545-05	Sample				8I29002	Due 10/30/08 - Return sample to box. See CL.
B8J0570-MS1	QC				8I29002	
B8J0570-MSD1	QC				8I29002	

Appendix E:

DFTPP Ion Abundance Criteria

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UMP006770

DFTPP Ion Abundance Criteria

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

Appendix F:

Quantitation Ions for Target Analytes

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Characteristic Ions for MDA1 Compounds

Parameter	Quantitation Ion	Identification Ions
Acetochlor	146	223, 162, 174
Alachlor	160	188, 146, 132
Atrazine	200	215, 202, 173
Chlorpyrifos	197	314, 199, 316
Cyanazine	225	240, 198, 172
Desethylatrazine	172	187, 174, 68
Deisopropylatrazine	68	158, 173, 44
Dimethenamid	154	230, 203, 138
EPTC	128	189, 86, 132
Ethafluralin	55	43, 276, 56
Fonofos	109	246, 137, 110
Metolachlor	162	238, 146, 163
Metribuzin	198	199, 74, 57
Pendimethalin	252	281, 192, 162
Phorate	75	260, 121, 97
Propachlor	120	176, 93, 77
Prometon	210	225, 168, 183
Propazine	214	229, 216, 172
Simazine	201	203, 186, 173
Terbufos	231	103, 97, 57
Triallate	86	268, 143, 128
Trifluralin	306	264, 145, 290
Internal Standards		
Trifluralin-d14	315	267, 163, 189
Surrogates		
Atrazine-d5	205	220, 207, 178
Diazinon-d10	183	314, 200, 232

All analytes are also compared to full reference spectra for identification.

Appendix G:

Acquisition Method/Operating Conditions

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TOPLEVEL PARAMETERS

```
Method Information For: C:\MSDCHEM\1\METHODS\2008MDAL1.M
Method Sections To Run:

  ( ) Save Copy of Method With Data
  ( ) MSTOP                Pre-Run Cmd/Macro  =
  ( ) Instrument Control   Pre-Run Cmd/Macro  =
  ( ) Data Analysis        Pre-Run Cmd/Macro  =
  (X) Data Acquisition
  ( ) Data Analysis
  ( ) MSTOP                Post-Run Cmd/Macro =
  ( ) Instrument Control   Post-Run Cmd/Macro =
  ( ) Data Analysis        Post-Run Cmd/Macro =
Method Comments:
  This is the default method
```

END OF TOPLEVEL PARAMETERS

INSTRUMENT CONTROL PARAMETERS

6890 GC METHOD

```
OVEN
   Initial temp:  55 'C (On)              Maximum temp:  360 'C
   Initial time:  1.00 min                Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp  Final time
      1 25.00     185         0.00
      2  7.50     245         0.00
      3 30.00     350         2.00
      4   0.0(Off)
   Post temp:  0 'C
   Post time:  0.00 min
   Run time:  19.70 min

FRONT INLET (SPLIT/SPLITLESS)           BACK INLET (UNKNOWN)
   Mode:  Pulsed Splitless
   Initial temp:  275 'C (On)
   Pressure:  8.03 psi (On)
   Pulse pressure:  40.0 psi
   Pulse time:  1.00 min
   Purge flow:  50.0 mL/min
   Purge time:  1.00 min
   Total flow:  52.9 mL/min
   Gas saver:  On
   Saver flow:  15.0 mL/min
   Saver time:  2.00 min
   Gas type:  Helium

COLUMN 1                                COLUMN 2
   Capillary Column                        (not installed)
   Model Number:  Zebro ZB-5
   5% Phenyl
   Max temperature:  360 'C
   Nominal length:  30.0 m
   Nominal diameter:  250.00 um
```

```
   Nominal film thickness:  0.50 um
   Mode:  constant flow
   Initial flow:  1.0 mL/min
   Nominal init pressure:  8.03 psi
   Average velocity:  37 cm/sec
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  vacuum

FRONT DETECTOR (NO DET)

SIGNAL 1
   Data rate:  20 Hz
   Type:  test plot
   Save Data:  Off
   Zero:  0.0 (Off)
   Range:  0
   Fast Peaks:  Off
   Attenuation:  0

BACK DETECTOR (NO DET)

SIGNAL 2
   Data rate:  20 Hz
   Type:  test plot
   Save Data:  Off
   Zero:  0.0 (Off)
   Range:  0
   Fast Peaks:  Off
   Attenuation:  0

COLUMN COMP 1
   (No Detectors Installed)

COLUMN COMP 2
   (No Detectors Installed)

THERMAL AUX 2
   Use:  MSD Transfer Line Heater
   Description:
   Initial temp:  315 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

POST RUN
   Post Time: 0.00 min

TIME TABLE
   Time       Specifier                    Parameter & Setpoint

                              7673 Injector

     Front Injector:
        Sample Washes                  0
        Sample Pumps                   4
        Injection Volume             1.0 microliters
        Syringe Size                10.0 microliters
        Nanoliter Adapter            Off
        PostInj Solvent A Washes       4
        PostInj Solvent B Washes       4
        Viscosity Delay                2 seconds
        Plunger Speed               Fast
        PreInjection Dwell          0.00 minutes
        PostInjection Dwell         0.02 minutes

     Back Injector:
No parameters specified

 Column 1 Inventory Number :
 Column 2 Inventory Number :

                              MS ACQUISITION PARAMETERS

General Information
------- -----------

Tune File                 : TUN9007.U
Acquistion Mode           : Scan
```

MS Information
-- -----------

Solvent Delay : 5.80 min

EM Absolute : False
EM Offset : 0
Resulting EM Voltage : 1305.9

[Scan Parameters]

Low Mass : 35.0
High Mass : 500.0
Threshold : 25
Sample # : 2 A/D Samples 4

[MSZones]

MS Quad : 150 C maximum 200 C
MS Source : 230 C maximum 250 C

END OF MS ACQUISITION PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

DATA ANALYSIS PARAMETERS

Method Name: C:\MSDCHEM\1\METHODS\2008MDAL1.M

Percent Report Settings

Sort By: Signal

Output Destination
Screen: Yes
Printer: Yes
File: No

Integration Events: AutoIntegrate

Generate Report During Run Method: No

Signal Correlation Window: 0.020

Qualitative Report Settings

Peak Location of Unknown: Apex

Library to Search Minimum Quality
DEMO.L 0

Integration Events: AutoIntegrate

Report Type: Summary

Output Destination
    Screen: Yes
    Printer: Yes
    File: No

Generate Report During Run Method: No

Quantitative Report Settings

Report Type: Summary

Output Destination
    Screen: Yes
    Printer: No
    File: No

Generate Report During Run Method: No

Calibration Last Updated:

Reference Window: 10.00 Percent
Non-Reference Window: 5.00 Percent
Correlation Window: 0.02 minutes
Default Multiplier: 1.00
Default Sample Concentration: 0.00

Compound Information

*** Empty Quantitation Database ***

END OF DATA ANALYSIS PARAMETERS

Thu Jan 15 10:34:51 2009

Additional Information for MDA1PLUS.M
File created Wed Apr 13 16:25:15 2005

Method : C:\MSDCHEM\1\METHODS\BMDAL1.M
Renamed: C:\MSDCHEM\1\METHODS\MDA1PLUS.M
Wed Apr 13 16:25:15 2005

Method : C:\MSDCHEM\1\METHODS\MDA1PLUS.M
Renamed: C:\MSDCHEM\1\METHODS\MDALIST1.M
Wed Apr 13 16:25:45 2005

Method : C:\MSDCHEM\1\METHODS\BMDALIST1.M
Renamed: C:\MSDCHEM\1\METHODS\MDALIST1.M
Wed Oct 12 07:39:45 2005

Method : C:\MSDCHEM\1\METHODS\MDALIST1.M
Renamed: C:\MSDCHEM\1\METHODS\2008MDAL1.M
Thu Oct 09 14:13:32 2008

Appendix H:

MDL/RL and Control Limits

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3/3/2009

Analytical Method Information

8270 MDA LIST 1 WATERS in Water (EPA 8270C)

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
EPTC	0.22	0.50 ug/L		30	65 - 115	30	65 - 115	30
Propachlor	0.14	0.50 ug/L		30	65 - 115	30	65 - 115	30
Ethalfluralin	0.47	0.50 ug/L		30	65 - 115	30	65 - 115	30
Deisopropylatrazine	0.26	0.50 ug/L		30	65 - 115	30	65 - 115	30
Trifluralin	0.21	0.50 ug/L		30	65 - 115	30	65 - 115	30
Desethylatrazine	0.29	0.50 ug/L		30	65 - 115	30	65 - 115	30
Phorate	0.58	1.0 ug/L		30	65 - 115	30	65 - 115	30
Prometon	0.29	0.50 ug/L		30	65 - 115	30	65 - 115	30
Simazine	0.32	0.50 ug/L		30	65 - 115	30	65 - 115	30
Atrazine	0.24	0.50 ug/L		30	65 - 115	30	65 - 115	30
Propazine	0.21	0.50 ug/L		30	65 - 115	30	65 - 115	30
Terbufos	0.54	1.0 ug/L		30	65 - 115	30	65 - 115	30
Fonofos	0.30	0.50 ug/L		30	65 - 115	30	65 - 115	30
Triallate	0.34	0.50 ug/L		30	65 - 115	30	65 - 115	30
Metribuzin	0.35	0.50 ug/L		30	65 - 115	30	65 - 115	30
Dimethenamid	0.24	0.50 ug/L		30	50 - 120	30	50 - 120	30
Acetochlor	0.25	0.50 ug/L		30	65 - 115	30	65 - 115	30
Alachlor	0.19	0.50 ug/L		30	65 - 115	30	65 - 115	30
Cyanazine	0.48	0.50 ug/L		30	65 - 115	30	65 - 115	30
Metolachlor	0.28	0.50 ug/L		30	65 - 115	30	65 - 115	30
Chlorpyrifos	0.34	0.50 ug/L		30	65 - 115	30	65 - 115	30
Pendimethalin	0.25	0.50 ug/L		30	65 - 115	30	65 - 115	30
surr: Atrazine-d5			50 - 120					
surr: Diazinon-d10			50 - 120					
Trifluralin-d14								

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Analytical Method Information

8270 MDA LIST 1 SOILS in Soil (EPA 8270C)

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
EPTC	0.0060	0.040 mg/kg		30	40 - 105	25	60 - 115	20
Propachlor	0.0090	0.040 mg/kg		30	55 - 110	25	75 - 115	20
Ethalfluralin	0.014	0.040 mg/kg		30	30 - 125	35	70 - 120	20
Deisopropylatrazine	0.0080	0.040 mg/kg		30	30 - 125	25	70 - 120	20
Trifluralin	0.014	0.040 mg/kg		30	30 - 120	35	80 - 115	20
Desethylatrazine	0.011	0.040 mg/kg		30	30 - 125	25	70 - 120	20
Phorate	0.0060	0.040 mg/kg		30	35 - 110	35	70 - 115	20
Prometon	0.0060	0.040 mg/kg		30	50 - 115	25	75 - 120	20
Simazine	0.0090	0.040 mg/kg		30	40 - 115	25	50 - 110	20
Atrazine	0.010	0.040 mg/kg		30	45 - 115	25	70 - 120	20
Propazine	0.0070	0.040 mg/kg		30	30 - 125	25	70 - 120	20
Terbufos	0.0090	0.040 mg/kg		30	30 - 125	35	70 - 115	20
Fonofos	0.0040	0.040 mg/kg		30	30 - 120	35	70 - 120	20
Triallate	0.0050	0.040 mg/kg		30	30 - 110	35	70 - 120	20
Metribuzin	0.0090	0.040 mg/kg		30	40 - 115	25	75 - 120	20
Dimethenamid	0.0060	0.040 mg/kg		30	55 - 110	25	70 - 120	20
Acetochlor	0.010	0.040 mg/kg		30	50 - 110	25	70 - 120	20
Alachlor	0.0070	0.040 mg/kg		30	40 - 110	25	75 - 120	20
Cyanazine	0.0080	0.040 mg/kg		30	30 - 125	25	70 - 120	20
Metolachlor	0.0030	0.040 mg/kg		30	40 - 115	25	70 - 120	20
Chlorpyrifos	0.0070	0.040 mg/kg		30	30 - 125	35	70 - 120	20
Pendimethalin	0.016	0.040 mg/kg		30	30 - 115	35	75 - 120	20
Metalaxyl	0.020	0.040 mg/kg		30	50 - 120	25	50 - 120	20
surr: Atrazine-d5			70 - 120					
surr: Diazinon-d10			50 - 120					
Trifluralin-d14								

DESCRIPTION:

Sample Preparation for MDA list 2 Pesticides in Soil Sample Matrices.

SUMMARY:

This procedure is used to prepare soil samples for the analysis of MDA list 2 Acid Herbicides. This procedure is based on EPA Method SW-846 8151A and EPA Method SW-846 3545. Because the List 2 herbicides are produced and used in various forms (i.e. acid, salt, ester, etc.), this method describes a hydrolysis step that can be used to convert herbicide esters into the acid form. The acids are then converted to their methyl esters using diazomethane as the derivatizing agent. The extract is concentrated to a 1mL final volume for analysis.

SCOPE:

This procedure complies with the requirements of the Resource Conservation and Recovery Act (RCRA). This SOP is applicable to the analysis of soil samples. This applies to the preparation portion only.

DOCUMENT CONTINUITY:

This SOP replaces MDA2SOILPREP revision 1.

SIGNATURES:

Quality Assurance [signature] Michelle M. Hubanks **Date** 5/19/09

Technical Lead [signature] Rupali Sawant **Date** 05/18/2009

Laboratory Manager [signature] Thomas P. Wagner **Date** 05/19/09

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1.0 PERSONNEL QUALIFICATIONS:

1.1 Personnel performing this procedure must be qualified per the requirements outlined in chapter 1 of the Analytical Laboratory Quality Assurance Manual (QAM).

2.0 SAFETY:

2.1 Personnel performing this procedure must follow general laboratory safety practices as defined in chapter 1 of the (QAM).

2.2 When working with organic compounds, wear solvent resistant gloves.

2.3 Diazomethane esterification can be hazardous. The diazomethane reagent is a carcinogen and a mutagen. Diazomethane can explode if exposed to heat or moisture. **Note:** when performing diazomethane esterification, be careful not to breathe the vapors. Perform in a hood and do not allow any contact with the skin.

2.4 A protective face shield should be worn during the diazomethane reagent generation.

3.0 DEFINITIONS:

3.1 Refer to standardized Braun Intertec Corporation definitions as described in chapter 4 of the QAM.

3.2 Leech Lodge: A small Styrofoam cooler that contains steel pellets used in the preparation of the diazomethane reagent.

3.3 KOH: Potassium hydroxide.

3.4 H_2SO_4: Sulfuric Acid.

3.5 UPDI: Ultra Pure Deionized Water

3.6 NaOH: Sodium Hydroxide.

3.7 NaCl: Sodium Chloride.

3.8 QA/QC: Refers to the Quality Group (Quality Director and QA Officer).

3.9 $MeCl_2$: Methylene Chloride.

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3.10 LIMS: Laboratory Information Management System.

3.11 Element: the LIMS used by the Analytical Laboratory.

4.0 FORMS & RECORDS:

4.1 LIMS Bench Sheet, Refer to Appendix A.

4.2 LIMS Standard Record, Refer to Appendix B.

5.0 EQUIPMENT & SUPPLIES:

5.1 Dionex ASE 200 Accelerated Solvent Extractor.

5.2 ASE Extraction Vessels.

5.3 Whatman D28 filters (19.8MM, p/n04958) or equivalent.

5.4 Separatory funnel: 2000 mL, Teflon.

5.5 Separatory funnel shaker – Braun design with 8 funnel capacity.

5.6 Erlenmeyer flask: 500 mL.

5.7 TurboVap II concentration work Station.

5.8 200 mL Zymark Turbovap II Concentrator tubes with a 1 mL reservoir.

5.9 Glass stir rods (used for breaking emulsions).

5.10 Diazomethane Generator Kit, Aldrich Chemical Cat # 210,025-0 or equivalent.

5.11 500 mL and 1000 mL Pyrex beakers.

5.12 Hot Plate with stirring mechanism.

5.13 HCl Rinsed Glass wool.

5.14 Thermometer, 1 degree gradients.

5.15 Disposable pipettes – 1 mL, 5 mL and 10 mL.

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6.0 REAGENTS & STANDARDS:

6.1 UPDI water: Ultra pure deionized water equivalent to ASTM type1.

6.2 Glacial Acetic Acid.

6.3 Methylene Chloride: Pesticide grade or equivalent.

6.4 Methanol: Pesticide grade or equivalent.

6.5 Acetone, pesticide grade.

6.6 Potassium hydroxide, ACS grade.

6.7 Ethanol, pesticide grade.

6.8 Ethyl ether, pesticide grade.

6.9 Diazald, Aldrich Chemical, 99+%.

6.10 Liquid N_2.

6.11 Sulfuric acid (12N) H_2SO_4. Slowly add 335 mL H_2SO_4 to 665 mL of UPDI water. This reagent will get very hot while being made and should be prepared in an Erlenmeyer flask placed in a cold water bath to minimize the hazard. Start by adding the acid to 500 mL of UPDI and bring up to a final volume of 1000 mL.

6.12 Sodium Hydroxide (6N) NaOH. This reagent will get very hot while being made and should be prepared in a cold water bath to minimize the hazard. Add 240 grams of NaOH to 800 mL UPDI water in a one liter volumetric flask. Bring to one liter final volume after adding all NaOH pellets.

6.13 Sodium chloride, ACS grade or equivalent.

6.14 Acidified Sodium Sulfate: (ACS) granular. Prepare a slurry using 1000 g sodium sulfate with enough ethyl ether to just cover the solid, then add 1 mL of concentrated sulfuric acid. Remove the ether under a vacuum or boil away on the steam bath. Mix 1 g of the resulting solid with 5 mL of UPDI water and measure the pH of the mixture. It must be below pH 5. Store in a sealed, dry container.

6.15 Diazomethane reagent – Prepared using the Diazomethane Generation Kit as described 6.14.1-6.14.4. All quantities of reagents may be doubled in order to

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generate a "double batch" of diazald solution. Note: Extreme care must be taken when performing this step as increasing the batch size increases the potential strength of explosion.

6.15.1 In the reaction vessel, add 10 mL of ethanol to a solution of 5 grams KOH in 8 mL of UPDI water. Attach a 100 mL receiving flask to the condenser and cool the receiver in a leech lodge (small Styrofoam cooler that contains steel pellets) that has been filled to the top of pellets with liquid N_2. Attach an ether trap containing approximately 2 mL of ethyl ether to the side arm.

6.15.2 Place the separatory funnel that comes with the Diazomethane Generation Kit over the reaction vessel and fill the funnel with a solution made up of 5 grams diazald in 45 mL ethyl ether. Shake gently or swirl to dissolve the diazald.

6.15.3 Warm the reaction vessel to 65°F and open the separatory funnel so that the rate of distillation is equal to the rate of addition. This rate should be a slow drip.

6.15.4 This reagent is good for approximately 14 days. Discard appropriately after this time.

6.16 Surrogate Solution – 100µg/mL of D.C.A.A.: Prepare by diluting the appropriate amount of stock solution to a 10mL final volume of acetone to achieve 100µg/mL D.C.A.A. Record standard preparation in the LIMS.

6.17 Spike Solution - 100µg/mL of List 2 analytes: Prepare by diluting the appropriate amount of stock solution(s) to a 10mL final volume of acetone to achieve 100µg/mL for each compound. Record standard preparation in the LIMS.

6.18 Hydrochloric acid (1N) - In a 1000ml volumetric flask, add 83mL HCl to 900mL UPDI. Bring to 1000 ml final volume with UPDI and invert several times to mix.

7.0 INTERFERENCES & PROCEDURAL LIMITATIONS:

7.1 Rinse all glassware with methylene chloride before use to ensure glassware is clean and free from contaminants.

7.2 Herbicides are acids and will react with alkaline substances, causing a loss during analysis. To avoid this problem all glassware and glass wool should be acid rinsed with 1N HCl. After the acid rinse, rinse the glassware 3 times with each UPDI water, acetone, and methylene chloride (any residual water on TurboVap tubes

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must be removed completely using acetone and methylene chloride as necessary). Sodium sulfate must also be acidified for this reason.

7.3 To avoid low recoveries, sample extracts must be dry prior to methylation.

8.0 SAMPLE ACCEPTANCE & HOLDING TIMES:

8.1 Samples must be stored at 4°C from the time of collection to the time of extraction.

8.2 Samples must be extracted within 14 days of sample collection and analyzed within 40 days of extraction.

9.0 CALIBRATION & STANDARDIZATION:

9.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for the calibration and standardization of the GC/MS.

10.0 PROCEDURE:

10.1 Record standard preparation in Element if new standards are needed.

10.1.1 Under Laboratory, click on Standards. Click Add.

10.1.2 For parent standards choose 1. "Specify each analyte and its concentration". Fill in the description, department, expiration date, initials and prepared date. Lot number and additional standard information can be typed in the comment section.

10.1.3 Choose the analytes from the analyte list. To narrow the list, select 8270 MDA List 2 Soil. Select the appropriate compounds from the list and add them to the standard.

10.1.4 Adjust the concentration and the concentration units as necessary.

10.1.5 Make sure the standard type is appropriate (i.e. for spike, click spike. For surrogate, click surrogate).

10.1.6 To prepare child standards click Add and choose 2. "Combine and/ or dilute existing standards."

10.1.7 Fill in the header information and choose the appropriate parent standard(s). Entering the standard volumes and the final volume will adjust

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the concentration of the child standard. It will not appear until the standard is saved.

10.1.8 Again, make sure the standard type is appropriate.

10.1.9 For standards that are created new but exactly the same as previous standards instead of choosing add, choose copy. The standard can be copied so that the analytes and concentrations do not need to be added. Fill in the header information with the correct preparation date and expiration date.

10.2 Create a new batch/bench sheet in Element.

10.2.1 Under Laboratory, click Batch. Click Add to create a new batch.

10.2.2 Choose the preparation method (EPA 3545), matrix and surrogate. Make sure the surrogate type is pre-prep. In the reagent box, right click and choose the appropriate solvents and reagents used for traceability.

10.2.3 Choose the appropriate analysis and click bench sheet.

10.2.4 On the bench sheet click edit and then add. Choose client samples (by container). Choose all of the samples that will be prepared in that batch. There cannot be more than 20 samples in each batch.

10.2.5 With each batch a MB, BS1, BSD1, MS1, MSD1 will be added. If there is insufficient sample for a MS/MSD pair a sample duplicate can be substituted. To remove QC or samples click on the appropriate sample and choose remove. To add QC click add and choose the appropriate QC sample.

10.2.6 To add information such as initial and final volumes, prepared date, prepared by and comments, highlight samples or QC, right click and choose the appropriate command. Be sure to adjust the sample volume to document the actual sample volume used in extraction.

10.2.7 The LCS/LCSD/MS/MSD standard ID can be added by right clicking on each QC sample and choosing the appropriate command. Also fill in the standards type (pre-prep) and the amount spiked. For sample duplicates and MS/MSD the sample source must also be added.

10.2.8 Print the bench sheet using the bch_std06.00.rpt.

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10.3 Prepare soil samples for ASE extraction.

10.3.1 Wash ASE Vessels with soap and water. Sonicate caps in $MeCl_2$ for 10 minutes. Rinse ASE Vessel with acetone to remove water, then with $MeCl_2$.

10.3.2 Acid rinse all ASE Collection Vials with 1 N HCl. After the acid rinse, rinse the glassware 3 times with each UPDI water and methylene chloride.

10.3.3 Weigh approximately 30 grams of sample into disposable weighing cup and record actual weight on the MDA list 2 Soils preparation bench sheet. Mix with enough diatomaceous earth to reduce clumping of wet soil/clay. For laboratory control samples (LCS/LCSD/MB) use 30 grams of Ottawa sand as the control matrix. Mix with diatomaceous earth. Record the weights on the bench sheet and enter the weights in the LIMS bench sheet.

10.3.4 Adjust the pH of the soil to 2 by adding approximately 0.5mL Acetic Acid to each soil sample in weighing cup. Mix well. Acetic Acid should be used instead of HCl as the HCl may damage the ASE Vessels.

10.3.5 Assemble ASE Extraction Vessels with grooved line at bottom, tightly twist cap onto bottom of vessel, and leave top off. Use plunger to insert filter into the bottom of the vessel. If sample is suspected to potentially clog the ASE, 2 or 3 filters may be used. Pour sample into Extraction Vessel. A metal funnel may be used to reduce spillage.

10.3.6 Deliver 50µL MDA list 2 surrogate to all samples, including quality control samples.

10.3.7 Deliver 50µL MDA list 2 spike to the LCS/LCSD and MS/MSD.

10.3.8 Tightly screw cap onto Extraction Vessel. Lable the vessel top caps with sample numbers and QC samples with ID. Load ASE Vessels and ASE Collection Vials into the ASE. Ensure that there is enough solvent for ASE instrument to complete the batch. Start ASE, using BNAOnly.sch schedule (90% MeCl2 and 10% acetone).

10.4 Prepare for Separatory Extraction.

10.4.1 When ASE extraction is finished, deliver contents from the ASE Collection Vial into pre-rinsed 2L separatory funnel with 1000mL of UPDI. Rinse Collection Vial twice with MeCl2, and twice with UPDI, adding all to separatory funnel.

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10.4.2 Add 250 grams of sodium chloride (NaCl) to each separatory funnel. Seal and shake each funnel to dissolve the salt. The salt may be added half at a time to make the shaking easier. The full 250 grams must be used in order to avoid low recoveries of select List 2 analytes.

10.5 Basic Portion of Extraction.

10.5.1 Adjust the pH of all samples and QC to greater than or equal to 12. To do this, add 5mL 6N NaOH solution, seal and shake. Confirm the pH using pH test strips for each sample before proceeding. Make a notation on the sample extraction form that the pH was adjusted. Some samples may have a greater buffering capacity requiring additional NaOH. If the pH is less than 12, add more 6N NaOH until a pH of greater than or equal to 12 is reached. Record any extra volume needed on the bench sheet.

10.5.2 Place separatory funnels on shaker and shake for 10 minutes.

10.5.3 Allow samples to stand for 1-2 hours at room temperature for hydrolysis to occur. Shake the separatory funnels by hand periodically during that timeframe.

10.5.4 Drain and discard $MeCl_2$ portion in appropriate waste container. Care must be taken to break up emulsions, but the emulsion phase should remain in the separatory funnel. In this initial step, it is important that none of the aqueous phase or emulsion is discarded. If necessary, the analyst should leave a small amount of methylene chloride in the separatory funnel from the clean up step. If the sample is very dirty or if there is a large emulsion, then a second or third shake with additional $MeCl_2$ may be employed for extra cleanup. Discard any additional $MeCl_2$ in an appropriate waste container.

10.6 Acidic portion of Extraction.

10.6.1 Adjust the pH to less than 2 by adding approximately 5mL of 12 N H_2SO_4. Check the pH and document the pH change on the extraction sheet. Add more 12 N H_2SO_4 if necessary. Record any extra volume needed on the bench sheet. Proceeding with the extraction with a pH of greater than 2 will significantly reduce recoveries.

10.6.2 Add 60 mL methylene chloride to each separatory funnel. Extract the sample by shaking the funnel for 2 minutes by hand with periodic venting to release pressure.

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10.6.3 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between the 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, but may include stirring, filtration of the emulsion through acidified glass wool, sonication or centrifugation. Collect the extract in a rinsed (7.2), 500 mL Erlenmeyer flask.

10.6.4 Extract the sample two more times using 60 mL of methylene chloride each time. Combine the extracts in the Erlenmeyer flask. Discard the water in the separatory funnel.

10.7 Dry sample extracts: Add acidified sodium sulfate to each Erlenmeyer flask to dry the extract. Samples should be allowed to stand for at least a 2 hour minimum with periodic swirling, overnight being preferred. If the sodium sulfate clumps, or forms a solid, more must be added until it remains free flowing. Removal of the water from the extract is a critical step, as any remaining water will interfere with the derivatization process. An acidified sodium sulfate powder funnel may also be useful in removal of water when transferring the extract to the Turbovap tube for concentration.

10.8 Concentrating the sample extracts.

10.8.1 Transfer the extract from the Erlenmeyer flask to a rinsed (7.2), 200 mL Turbovap tube being careful to avoid transferring any sodium sulfate, which can act as a boiling stone during concentration. Rinse the Erlenmeyer three times with methylene chloride, transferring the rinse to the Turbovap tube.

10.8.2 Concentrate the samples to approximately 500 µL using the Turbovap II at 40°C with enough N_2 pressure to swirl, but not splash the extract in the tube. The pressure needed to cause the contents to swirl may change as the volume of solvent in the Zymark tube decreases.

10.9 Esterification Process.

10.9.1 Add approximately 1.5 mL diazomethane reagent to each sample tube. Swirl by hand for one minute. Allow to stand for 30+ minutes with occasional swirling. If the yellow color persists and no bubbles are being generated, the derivatization is complete. If the yellow color is not present, the diazald has been consumed and more must be added until the yellow color persists.

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10.9.2 All samples in a batch must be derivatized with the same batch of diazomethane, since the efficiency of the derivatizing agent varies from batch to batch and decreases over time.

10.10 Final transfer: If the sample extract has not already concentrated down to 500ul through evaporation, reduce the sample volume to approximately 500 µL by allowing the solvent to evaporate spontaneously at room temperature to remove excess ether/diazomethane. Alternatively, use a slow stream of Nitrogen gas to concentrate the extract to approximately 500 µL in a water bath at 35°C. Using a 1 ml graduated pipette, bring up to a1mL volume with methylene chloride and transfer sample to an amber GC vial and crimp for analysis.

11.0 CALCULATIONS:

11.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for all applicable calculations

12.0 DATA REDUCTION & RECORDS:

12.1 All records must be completed at the time of sample preparation. Document all out of the ordinary information on the extraction worksheet such as a sample with high sediment content or strong odor.

12.2 Extraction paperwork is delivered to the analytical group and the samples are delivered to the GC/MS analyst or stored in the sample preparation laboratory refrigerator freezer door.

12.3 Once the analysis is complete the GC/MS analyst electronically transfers the data into the LIMS, creates a data packet that includes all applicable forms and raw data and submits data to an authorized technical peer for data verification. Refer to the SOP GCMS8270MDAL2 for more detail.

13.0 REPORTING:

13.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for information regarding reporting.

14.0 QUALITY CONTROL:

14.1 Batch QC Frequency:

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14.1.1 Batch QC generally consists of a MB, LCS, LCSD, MS and MSD with each set of 20 or fewer samples prepared together.

14.1.2 In situations when insufficient sample is received for MS and MSD a sample duplicate may be substituted for the MSD.

14.1.3 Each client sample and all QC samples are spiked with a surrogate solution to determine extraction efficiency.

14.2 Acceptance Limits for Batch QC:

14.2.1 Please refer to SOP GCMS8270MDAL2 for the batch QC limits.

14.3 Corrective Action for Batch QC:

14.3.1 If the MB, LCS, LCSD or the RPD between the LCS and LCSD are outside of acceptance limits then the batch must be re-extracted and reanalyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

14.3.2 If the MS/MSD, including the RPD between the MS/MSD is outside the acceptance limits then the data associated with the project from which that MS/MSD originated must be appropriately qualified. This assumes that the QC in 14.3.1 is within acceptance limits. If any of the QC is outside of acceptance, follow the current non-conformance procedure as is outlined in the QAM.

14.3.3 If the sample surrogates are outside of acceptance limits the specific sample must be re-extracted and re-analyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

15.0 METHOD PERFORMANCE:

15.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for all applicable method performance.

16.0 DETECTION LIMITS:

16.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for all applicable detection and reporting limits.

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17.0 REFERENCES:

17.1 PRIMARY REFERENCES:

17.1.1 US EPA SW-846 Method 8151A.

17.2 SECONDARY REFERENCES:

17.2.1 US EPA SW-846 Method 3545.

18.0 WASTE MANAGEMENT & POLLUTION PREVENTION:

18.1 Please refer to the general policies and procedures outlined in chapter 7 of the QAM regarding waste management and pollution prevention.

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Appendix A

Preparation Bench Sheet

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PREPARATION BENCH SHEET

B8J0446

Braun Intertec Corporation

Analysis: LIST 2 SOILS

Logbook:

Matrix: Soil

Analyst: RSS

Printed: 5/7/2009 10:06:34AM

Prepared using: ENVSVOCGCMS - EPA 3545

Surrogate ID: 8H13009

Lab Number	Prepared	Initial (g)	Final (mL)	Spike ID	uL Spike	Source ID	uL Surrogate	Position	Extraction Comments
0806433-01	10/20/08 11:34	30.26	1				50		
0806433-02	10/20/08 11:34	30.27	1				50		
0806433-03	10/20/08 11:34	30.41	1				50		
0806433-04	10/20/08 11:34	30.42	1				50		
B8J0446-BLK1	10/20/08 11:34	30.44	1				50		
B8J0446-BS1	10/20/08 11:34	30.31	1	8B25013	50		50		
B8J0446-BSD1	10/20/08 11:34	30.17	1	8B25013	50		50		
B8J0446-MS1	10/20/08 11:34	30.3	1	8B25013	50	0806433-01	50		
B8J0446-MSD1	10/20/08 11:34	30.16	1	8B25013	50	0806433-01	50		

Reagent	Description
6D27002	Acetic Acid - Glacial
8B25013	MDA L2 spike std. 100UG/ML
8E16023	Acidified Sodium Sulfate
8H07002	Diatomaceous Earth
8H13009	MDA L2 Surrogate std. (DCAA)
8H22033	Ottawa Sand
8I11021	NaCl
8I29042	Acetone Pesticide Grade
8J03016	Methylene Chloride
8J06018	12 N H2SO4
8J06026	6N NaOH
8J17017	Diazomethane

Appendix B

Analytical Standard Record

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Analytical Standard Record

Braun Intertec Corporation

9D29022

Description:	List 2 spike	Expires:	10/26/09
Standard Type:	Surrogate Spike	Prepared:	04/29/09
Solvent:	-	Prepared By:	Rupali Sawant
Final Volume (mls):	25	Department:	ENVSVOCGCMS
Vials:	1	Last Edit:	05/01/09 12:05 by MEF

5 ml of 9C24022 diluted to 25 ml with Acetone (# 9D03017)

Analyte	CAS Number	Concentration	Units
Triclopyr	55336-06-3	20	ug/mL
Picloram	1918-02-1	20	ug/mL
Pentachlorophenol	87-86-5	20	ug/mL
M.C.P.A.	94-74-6	20	ug/mL
Dinoseb	88-85-7	20	ug/mL
Dicamba	1918-00-9	20	ug/mL
Bentazon	25057-89-0	20	ug/mL
2,4-D.B.	94-82-6	20	ug/mL
2,4-D	94-75-7	20	ug/mL
2,4,5-T.P.	93-72-1	20	ug/mL
2,4,5-T	93-76-5	20	ug/mL

Parent Standards used in this standard:

Standard	Description	Prepared	Prepared By	Expires	Last Edit	(mls)
9C24022	MDA L2 spike std. 100UG/ML	03/24/09	Rupali Sawant	03/24/10	05/01/09 12:05 by MEF	5

Reviewed By Date

UMP006799

DESCRIPTION:

Sample Preparation for MDA List 2 Pesticides in Solid Sample Matrices using Solvent Extraction by Microwave.

SUMMARY:

This procedure is used to prepare solid samples for the analysis of MDA List 2 acid herbicides. It is based on EPA Methods SW-846 8151A and SW-846 3546. A 15 gram sample is dried using diatomaceous earth and extracted with a 50% methylene chloride and 50% acetone mixture using the CEM Mars Xpress Microwave system. Because the List 2 herbicides are produced and used in various forms (i.e. acid, salt, ester, etc.), this method describes a hydrolysis step that is used to convert herbicide esters into the acid form. The acids are then converted to their methyl esters using diazomethane as the derivatizing agent. The extract is concentrated to a 1mL final volume using the Zymark TurboVap concentration station.

SCOPE:

This procedure complies with the requirements of the Resource Conservation and Recovery Act (RCRA). This SOP is applicable to the preparation of solid samples using microwave extraction.

DOCUMENT CONTINUITY:

This SOP is an original SOP.

SIGNATURES:

Quality Assurance [signature] **Date** 4/1/09
Michelle Hubanks

Technical Lead Rebecca Bilek **Date** 4/1/09
Rebecca Bilek, Ph.D.

Laboratory Manager [signature] **Date** 04/01/09
Thomas P. Wagner

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1.0 PERSONNEL QUALIFICATIONS:

1.1 Personnel performing this procedure must be qualified per the requirements outlined in chapter 1 of the Analytical Laboratory Quality Assurance Manual (QAM).

2.0 SAFETY:

2.1 Personnel performing this procedure must follow general laboratory safety practices as defined in chapter 1 of the (QAM).

2.2 When working with organic compounds, wear solvent resistant gloves.

2.3 Follow standard laboratory safety procedures. Always wear a lab coat and safety glasses.

2.4 Review all Material Safety Data Sheets for chemicals used in this procedure.

2.5 Diazomethane esterification can be hazardous. The diazomethane reagent is a carcinogen and a mutagen. Diazomethane can explode if exposed to heat or moisture. **Note:** when performing diazomethane esterification, be careful not to breathe the vapors. Perform in a hood and do not allow any contact with the skin.

2.6 A protective face shield should be worn during the diazomethane reagent generation.

3.0 DEFINITIONS:

3.1 Refer to standardized Braun Intertec Corporation definitions as described in chapter 4 of the QAM.

3.2 TurboVap tubes: Zymark TurboVap 200 mL concentration tubes.

3.3 Leech Lodge: A small Styrofoam cooler that contains steel pellets used in the preparation of the diazomethane reagent.

3.4 KOH: Potassium hydroxide.

3.5 H_2SO_4: Sulfuric Acid.

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3.6 UPDI: Ultra Pure Deionized Water

3.7 NaOH: Sodium Hydroxide.

3.8 NaCl: Sodium Chloride.

3.9 QA/QC: Refers to the Quality Group (Quality Director and QA Officer).

3.10 $MeCl_2$: Methylene Chloride.

3.11 LIMS: Laboratory Information Management System.

3.12 Element: the LIMS used by the Analytical Laboratory.

4.0 FORMS & RECORDS:

4.1 LIMS Bench Sheet, Refer to Appendix A.

4.2 LIMS Standard Record, Refer to Appendix B.

5.0 EQUIPMENT & SUPPLIES:

5.1 CEM MARS5 Xpress Accelerated Reaction System, Model #907501, including solvent sensor assembly installed in exhaust line.

5.1.1 MARS Xpress Vessels, 75mL with stoppers and caps.

5.1.2 Vessel turntable, 40 position with composite sleeves for each position.

5.1.3 MARS Xpress vessel capping station.

5.1.4 Computer with Synergy Prep Software, version 3.32.

5.1.5 Microwave vessel racks.

5.1.6 Turntable assembly and filter funnels for filtering extract.

5.2 Graduated pipets: 1 mL, 5 mL and 10 mL.

5.3 Crimp top vials and PTFE crimp caps.

5.4 Zymark TurboVap Concentration Station.

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5.5 Zymark TurboVap 200 mL Concentration tubes.

5.6 Pyrex beakers: 50 mL, 500 mL and 1000 mL.

5.7 Erlenmeyer flasks: 250 mL, 500 mL and 1000 mL.

5.8 Analytical balance.

5.9 Filter paper, porosity: coarse, flow rate: fast, diameter: 18.5 cm (Fisher 0-790-G, or equivalent).

5.10 Powder funnels.

5.11 Separatory funnel: 2000 mL, Teflon.

5.12 Separatory funnel shaker – Braun design with 8 funnel capacity.

5.13 Erlenmeyer flask: 500 mL.

5.14 TurboVap II concentration work Station.

5.15 200 mL Zymark Turbovap II Concentrator tubes with a 1 mL reservoir.

5.16 Glass stir rods (used for breaking emulsions).

5.17 Diazomethane Generator Kit, Aldrich Chemical Cat # 210,025-0 or equivalent.

5.18 Hot Plate with stirring mechanism.

5.19 HCl Rinsed Glass wool.

5.20 Thermometer, with 1 degree gradients.

6.0 REAGENTS & STANDARDS:

6.1 UPDI water: Ultra pure deionized water equivalent to ASTM type1.

6.2 Glacial Acetic Acid (Fisher Biotech, Cat. #BP2401-212, or equivalent).

6.3 Methylene Chloride, $MeCl_2$, pesticide grade (Mallinckrodt, Cat. #H485-10, or equivalent).

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6.4 Methanol, CH_3OH, pesticide grade (Fisher Scientific, Cat. #A457-4, or equivalent).

6.5 Acetone, pesticide grade (Fisher Scientific, Cat. #A40-4, or equivalent).

6.6 Ottawa Sand (Fisher Scientific, Cat. #S23-3, or equivalent).

6.7 Potassium hydroxide, KOH, ACS grade (Fisher Scientific, Cat. #P250-3, or equivalent).

6.8 Ethanol, pesticide grade (Fisher Scientific, Cat. #A407-4, or equivalent).

6.9 Ethyl ether, pesticide grade (Fisher Scientific, Cat. #E199-4, or equivalent).

6.10 Diazald, 99+% (Aldrich Chemical, Cat. #D2,800-0, or equivalent).

6.11 Liquid N_2.

6.12 Sulfuric acid (12N) H_2SO_4. Slowly add 335 mL of concentrated H_2SO_4 to 665 mL of UPDI water. This reagent will get very hot while being made and should be prepared in an Erlenmeyer flask placed in a cold water bath to minimize the hazard. Start by adding the acid to 500 mL of UPDI and bring up to a final volume of 1000 mL.

6.13 Sodium Hydroxide (6N) NaOH. This reagent will get very hot while being made and should be prepared in a cold water bath to minimize the hazard. Add 240 grams of NaOH to 800 mL UPDI water in a one liter volumetric flask. Bring to one liter final volume after adding all NaOH pellets.

6.14 Sodium chloride, NaCl, ACS grade or equivalent.

6.15 Acidified Sodium Sulfate: (ACS) granular, 10-60 mesh, anhydrous (Fisher Scientific, Cat. #S415-200, or equivalent), purified by heating to 450°C for two hours. To acidify, prepare a slurry using 1000 g sodium sulfate in a large glass rectangular container. Add enough ethyl ether to just cover the solid, then add 1 mL of concentrated sulfuric acid. Stir with a glass stirring rod to mix. Let stand in a hood until all excess solvent evaporates. Mix 1 g of the resulting solid with 5 mL of UPDI water and measure the pH of the mixture. It must be below pH 5. Store in a sealed, dry container like a capped amber colored jar.

6.16 Diazomethane reagent – Prepared using the Diazomethane Generation Kit as described 6.14.1-6.14.4. All quantities of reagents may be doubled in order to

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generate a "double batch" of diazald solution. Note: Extreme care must be taken when performing this step as increasing the batch size increases the potential strength of explosion.

6.16.1 In the reaction vessel, add 10 mL of ethanol to a solution of 5 grams KOH in 8 mL of UPDI water. Attach a 100 mL receiving flask to the condenser and cool the receiver in a leech lodge (small Styrofoam cooler that contains steel pellets) that has been filled to the top of pellets with liquid N_2. Attach an ether trap containing approximately 2 mL of ethyl ether to the side arm.

6.16.2 Place the separatory funnel that comes with the Diazomethane Generation Kit over the reaction vessel and fill the funnel with a solution made up of 5 grams diazald in 45 mL ethyl ether. Shake gently or swirl to dissolve the diazald.

6.16.3 Warm the reaction vessel to 65°F and open the separatory funnel so that the rate of distillation is equal to the rate of addition. This rate should be a slow drip.

6.16.4 This reagent is good for approximately 14 days. Discard appropriately after this time.

6.17 Surrogate Solution – 100µg/mL of D.C.A.A.: Prepare by adding the appropriate amount of stock solution to a 10 mL final volume of acetone in a volumetric flask to achieve 100µg/mL D.C.A.A. Record standard preparation in the LIMS.

6.18 Spike Solution - 100µg/mL of List 2 analytes: Prepare by adding the appropriate amount of stock solution(s) to a 10 mL final volume of acetone in a volumetric flask to achieve 100µg/mL for each compound. Record standard preparation in the LIMS.

6.19 Hydrochloric acid (1N) - In a 1000 mL volumetric flask, add 83mL HCl to 900mL UPDI. Bring to volume with UPDI and invert several times to mix.

7.0 INTERFERENCES & PROCEDURAL LIMITATIONS:

7.1 Rinse all glassware with methylene chloride before use to ensure glassware is clean and free from contaminants.

7.2 Herbicides are acids and will react with alkaline substances, causing a loss during analysis. To avoid this problem all glassware and glass wool should be acid rinsed with 1N HCl. After the acid rinse, rinse the glassware 3 times with each UPDI

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water, acetone, and methylene chloride (any residual water on TurboVap tubes must be removed completely using acetone and methylene chloride as necessary). Sodium sulfate must also be acidified for this reason.

7.3 To avoid low recoveries, sample extracts must be dry prior to methylation.

7.4 Refer to SOP GCMS8270MDAL2 for analytical interferences.

8.0 SAMPLE ACCEPTANCE & HOLDING TIMES:

8.1 Samples must be stored at 4°C from the time of collection to the time of extraction.

8.2 Samples must be extracted within 14 days of sample collection and analyzed within 40 days of extraction.

9.0 CALIBRATION & STANDARDIZATION:

9.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for the calibration and standardization of the GC/MS.

10.0 PROCEDURE:

10.1 Record standard preparation in Element if new standards are needed.

10.1.1 Under Laboratory, click on Standards. Click Add.

10.1.2 For parent standards choose 1. "Specify each analyte and its concentration". Fill in the description, department, expiration date, initials and prepared date. Lot number and additional standard information can be typed in the comment section.

10.1.3 Choose the analytes from the analyte list. To narrow the list, select 8270 MDA List 2 Soil. Select the appropriate compounds from the list and add them to the standard.

10.1.4 Adjust the concentration and the concentration units as necessary.

10.1.5 Make sure the standard type is appropriate (i.e. for spike, click spike. For surrogate, click surrogate).

10.1.6 To prepare child standards click Add and choose 2. "Combine and/ or dilute existing standards."

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10.1.7 Fill in the header information and choose the appropriate parent standard(s). Entering the standard volumes and the final volume will adjust the concentration of the child standard. It will not appear until the standard is saved.

10.1.8 Again, make sure the standard type is appropriate.

10.1.9 For standards that are created new but exactly the same as previous standards instead of choosing add, choose copy. The standard can be copied so that the analytes and concentrations do not need to be added. Fill in the header information with the correct preparation date and expiration date.

10.2 Create a new batch/bench sheet in Element.

10.2.1 Under Laboratory, click Batch. Click Add to create a new batch.

10.2.2 Choose the preparation method (EPA 3546), matrix and surrogate. Make sure the surrogate type is pre-prep. In the reagent box, right click and choose the appropriate solvents and reagents used for traceability.

10.2.3 Choose the appropriate analysis and click bench sheet.

10.2.4 On the bench sheet click edit and then add. Choose client samples (by container). Choose all of the samples that will be prepared in that batch. There cannot be more than 20 samples in each batch.

10.2.5 With each batch a BL1, BS1, BSD1, MS1, MSD1 will be added. If there is insufficient sample for a MS/MSD pair a sample duplicate can be substituted. To remove QC or samples click on the appropriate sample and choose remove. To add QC click add and choose the appropriate QC sample.

10.2.6 To add information such as initial and final volumes, prepared date, prepared by and comments, highlight samples or QC, right click and choose the appropriate command. Be sure to adjust the sample volume to document the actual sample volume used in extraction.

10.2.7 The BS/BSD/MS/MSD standard ID can be added by right clicking on each QC sample and choosing the appropriate command. Also fill in the standards type (pre-prep) and the amount spiked. For sample duplicates and MS/MSD the sample source must also be added.

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10.2.8 Print the bench sheet using the bch_std 06.00.rpt.

10.3 All extraction glassware and vessels (50 mL beakers, 250 mL Erlenmeyer flasks, microwave vessels, etc.) must be rinsed with 1N HCl. After the acid rinse, rinse the glassware 3 times with each UPDI water, acetone, and methylene chloride (any residual water on TurboVap tubes must be removed completely using acetone and methylene chloride as necessary).

10.4 Prepare samples for extraction.

10.4.1 Weigh approximately 15 grams of each sample into a 50 mL beaker. Document the actual sample weight on the bench sheet.

10.4.2 For laboratory control samples (BS/BSD/BLK) use 15 grams of Ottawa sand.

10.4.3 Adjust the pH of the soil to 2 by adding approximately 0.5mL Acetic Acid to each soil sample. Mix well.

10.4.4 Deliver 50µL MDA List 2 surrogate to all samples, including quality control samples.

10.4.5 Deliver 50µL MDA List 2 spike to the BS/BSD and MS/MSD.

10.4.6 Mix with diatomaceous earth until free flowing to absorb moisture from the sample. In order to achieve optimal recoveries, it is important to make sure the sample is free flowing.

10.4.7 Add 5 g of solid acidified sodium sulfate to each sample (including QC samples) and mix.

10.4.8 Pour the sample mixed with diatomaceous earth and sodium sulfate into the vessel using a powder funnel. Organize vessels in the vessel rack and make a note of the position of each in the rack.

10.4.9 Dispense 15 mL of $MeCl_2$ into the beaker after the soil has been transferred to rinse the beaker. Add the rinsing solvent to the vessel using the powder funnel, rinsing the funnel as the solvent is added. Repeat with 15 mL of acetone.

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10.5 Stopper and cap each vessel. Start the cap by hand to make sure the threads are aligned correctly and finish using the Vessel Capping Station, which will result in all vessels being capped uniformly. Shake each vessel well to mix the contents.

10.6 Put the vessels in the turntable, labeling the turntable position of each on the bench sheet. It is important to distribute the vessels around the turntable instead of bunching them all together.

10.7 Load the turntable containing the microwave vessels into the microwave. The turntable will lock in place when aligned correctly.

10.8 Select the method in the CEM Synergy Prep software for organic extraction based on the number of vessels that will be processed together. For 6 to 10 vessels, select the method "400 Org Extraction", for 11 to 20 vessels use "800 Org Extraction", and for more than 20 vessels use "1600 Org Extraction". All of the methods are identical except for the power (in watts).

10.8.1 The required parameters for the extraction of organic compounds from soil samples are listed in Table 1 below.

Table 1: Extraction Parameters	
Parameters	**MDA List 2**
Control style	Ramp to Temperature
Vessel type	Xpress
Reaction type	organic
Power (watts)	400, 800, or 1600
%Power	100
Time to ramp to temperature	10:00 minutes
Temperature	110°C
Hold time	20:00 minutes

10.8.2 After the correct method is selected in the software, click "run method" or "start".

10.9 Allow the vessels to cool completely (inside or outside the unit) before proceeding.

10.10 Collection and filtering of sample extracts.

10.10.1 After the vessels are at room temperature, remove each from the turntable and organize in the vessel rack. While transferring the vessels to the rack, shake the vessel to loosen the soil. This will aid in transferring the contents.

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10.10.2 Use the vessel capping station in reverse mode to loosen each vessel cap.

10.10.3 Decant the liquid portion in each vessel into a filter assembly consisting of a 250 mL Erlenmeyer flask (rinsed with 1N HCl, followed by rinsing 3 times with each UPDI water, acetone, and methylene chloride), positioned in the turntable with a filter funnel over the mouth and a piece of filter paper (folded into eighths) inside the funnel.

10.10.4 Wait until after the extract has almost finished passing through the filter before adding the soil sample to avoid splashing. Rinse the vessel with two 15mL portions of $MeCl_2$, using each to rinse the soil in the filter paper of residual analytes.

10.10.5 Add a 15 mL portion of $MeCl_2$ directly to the filter to again rinse the soil sample.

10.10.6 When all of the solvent has passed through the filter paper into the flask, deliver the extract into a pre-rinsed 2L separatory funnel containing 1000mL of UPDI. Rinse the flask twice with $MeCl_2$, and twice with UPDI, adding all to the separatory funnel.

10.10.7Add 250 grams of sodium chloride (NaCl) to each separatory funnel. Seal and shake each funnel to dissolve the salt. The salt may be added half at a time to make the shaking easier. The full 250 grams must be used in order to avoid low recoveries of select List 2 analytes.

10.11 Basic Portion of Extraction.

10.11.1Adjust the pH of all samples and QC to greater than or equal to 12. To do this, add 5mL 6N NaOH solution, seal and shake. Confirm the pH using test strips for each sample before proceeding. Make a notation on the sample extraction form that the pH was adjusted. Some samples may have a greater buffering capacity requiring additional NaOH. If the pH is less than 12, add more 6N NaOH until a pH of greater than or equal to 12 is reached. Record any extra volume needed on the bench sheet.

10.11.2Place separatory funnels on shaker and shake for 10 minutes.

10.11.3Allow samples to stand for 1-2 hours at room temperature for hydrolysis to occur. Shake the separatory funnels by hand periodically during that timeframe.

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10.11.4 Drain and discard $MeCl_2$ portion in appropriate waste container. Care must be taken to break up emulsions, but the emulsion phase should remain in the separatory funnel. In this initial step, it is important that none of the aqueous phase or emulsion is discarded. If necessary, the analyst should leave a small amount of methylene chloride in the separatory funnel from the clean up step. If the sample is very dirty or if there is a large emulsion, then a second or third shake with additional $MeCl_2$ may be employed for extra cleanup.

10.12 Acidic portion of Extraction.

10.12.1 Adjust the pH to less than 2 by adding approximately 5mL of 12 N H_2SO_4. Check the pH and document the pH change on the extraction sheet. Add more 12 N H_2SO_4 if necessary. Record any extra volume needed on the bench sheet. Proceeding with the extraction with a pH of greater than 2 will significantly reduce recoveries.

10.12.2 Add 60 mL $MeCl_2$ to each separatory funnel. Extract the sample by shaking the funnel for 2 minutes by hand with periodic venting to release pressure.

10.12.3 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between the 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, but may include stirring, filtration of the emulsion through acidified glass wool, sonication or centrifugation. Collect the extract in a 500 mL Erlenmeyer flask.

10.12.4 Extract the sample two more times using 60 mL of methylene chloride each time. Combine the extracts in the Erlenmeyer flask. Discard the water in the separatory funnel.

10.13 Dry sample extracts: Add acidified sodium sulfate to each Erlenmeyer flask to dry the extract. Samples should be allowed to stand for at least a 2 hour minimum with periodic swirling, overnight being preferred. If the sodium sulfate clumps, or forms a solid, more must be added until it remains free flowing. Removal of the water from the extract is a critical step, as any remaining water will interfere with the derivatization process. An acidified sodium sulfate powder funnel may also be useful in removal of water when transferring the extract to the Turbovap tube for concentration.

10.14 Concentrating the sample extracts.

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10.14.1 Transfer the extract from the Erlenmeyer flask to a rinsed 200 mL Turbovap tube being careful to avoid transferring any sodium sulfate, which can act as a boiling stone during concentration. Rinse the Erlenmeyer three times with methylene chloride, transferring the rinse to the Turbovap tube.

10.14.2 Concentrate the samples to approximately 200 µL using the Turbovap II at 42°C with enough N_2 pressure to swirl, but not splash the extract in the tube. The pressure needed to cause the contents to swirl may change as the volume of solvent in the Zymark tube decreases.

10.15 Esterification Process.

10.15.1 Add approximately 1.5 mL diazomethane reagent to each sample tube. Swirl by hand for one minute. Allow to stand for 30+ minutes with occasional swirling. If the yellow color persists and no bubbles are being generated, the derivatization is complete. If the yellow color is not present, the diazald has been consumed and more must be added until the yellow color persists.

10.15.2 All samples in a batch must be derivatized with the same batch of diazomethane, since the efficiency of the derivatizing agent varies from batch to batch and decreases over time.

10.16 Final transfer: If the sample extract has not already concentrated down to 200ul through evaporation, reduce the sample volume to approximately 200 µL by allowing the solvent to evaporate spontaneously at room temperature to remove excess ether/diazomethane. Alternatively, use a slow stream of Nitrogen gas to concentrate the extract to approximately 200 µL in a water bath at 35°C. Bring up to a 1mL volume with methylene chloride and transfer sample to an amber GC vial and crimp for analysis.

11.0 CALCULATIONS:

11.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for all applicable calculations

12.0 DATA REDUCTION & RECORDS:

12.1 Complete a Track-IT! if required and route to QA/QC.

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12.2 Once the analysis is complete the GC/MS analyst electronically transfers the data into the LIMS, creates a data packet that includes all applicable forms and raw data and submits data to an authorized technical peer for data verification. Refer to the SOP GCMS8270MDAL2 for more detail.

12.3 All records must be completed at the time of sample preparation. Document all out of the ordinary information on the bench sheet such as a sample with a strong odor.

12.4 Extraction paperwork is delivered to the analytical group and the samples are delivered to the GC/MS analyst or stored in the door of the freezer compartment in the refrigerator in the sample preparation laboratory.

13.0 REPORTING:

13.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for information regarding reporting.

14.0 QUALITY CONTROL:

14.1 Batch QC Frequency:

14.1.1 Batch QC generally consists of a BLK, BS, BSD, MS and MSD with each set of 20 or fewer samples prepared together.

14.1.2 In situations when insufficient sample is received for MS and MSD a sample duplicate may be substituted for the MSD.

14.1.3 Each client sample and all QC samples are spiked with a surrogate solution to determine extraction efficiency.

14.2 Acceptance Limits for Batch QC:

14.2.1 Please refer to SOP GCMS8270MDAL2 for the batch QC limits.

14.3 Corrective Action for Batch QC:

14.3.1 If the BLK, BS, or BSD recoveries or the RPD between the BS and BSD are outside of acceptance limits then the batch must be re-extracted and reanalyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of

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acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

14.3.2 If the MS/MSD, including the RPD between the MS/MSD is outside the acceptance limits then the data associated with the project from which that MS/MSD originated must be appropriately qualified. This assumes that the QC in 14.3.1 is within acceptance limits. If any of the QC is outside of acceptance, follow the current non-conformance procedure as is outlined in the QAM.

14.3.3 If the sample surrogates are outside of acceptance limits the specific sample must be re-extracted and re-analyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

15.0 METHOD PERFORMANCE:

15.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for all applicable method performance.

16.0 DETECTION LIMITS:

16.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL2 for all applicable detection and reporting limits.

17.0 REFERENCES:

17.1 PRIMARY REFERENCES:

17.1.1 US EPA SW-846 Method 8151A.

17.2 SECONDARY REFERENCES:

17.2.1 US EPA SW-846 Method 3545.

18.0 WASTE MANAGEMENT & POLLUTION PREVENTION:

18.1 Please refer to the general policies and procedures outlined in chapter 7 of the QAM regarding waste management and pollution prevention.

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Appendix A

Preparation Bench Sheet

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PREPARATION BENCH SHEET

B8K0085

Braun Intertec Corporation

Analysis: LIST 2 SOILS
Logbook:
Matrix: Soil

Analyst: RSS
Printed: 4/1/2009 9:38:01AM
Surrogate ID: 8H13009

Prepared using: ENVSVOCGCMS - EPA 3545

Lab Number	Prepared	Initial (g)	Final (mL)	Spike ID	uL Spike	Source ID	uL Surrogate	Position	Extraction Comments
0806615-01	11/05/08 11:10	30.31	1				50		
B8K0085-BLK1	11/05/08 11:10	30.09	1				50		
B8K0085-BS1	11/05/08 11:10	30.47	1	8B25013	50		50		
B8K0085-BSD1	11/05/08 11:10	30.04	1	8B25013	50		50		
B8K0085-MS1	11/05/08 11:10	30.36	1	8B25013	50	0806615-01	50		
B8K0085-MSD1	11/05/08 11:10	30.32	1	8B25013	50	0806615-01	50		

Reagent	Description
8B25013	MDA L2 spike std. 100UG/ML
8E16023	Acidified Sodium Sulfate
8F12063	Acetic Acid, Glacial
8H13009	MDA L2 Surrogate std. (DCAA)
8H22033	Ottawa Sand
8I11021	NaCl
8I29042	Acetone Pesticide Grade
8J06018	12 N H2SO4
8J06026	6N NaOH
8J17017	Diazomethane
8J24001	Methylene Chloride

Appendix B

Analytical Standard Record

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Analytical Standard Record

Braun Intertec Corporation

9C24022

Description:	MDA L2 spike std. 100UG/ML	Expires:	03/24/10
Standard Type:	Analyte Spike	Prepared:	03/24/09
Solvent:	Acetone	Prepared By:	Rupali Sawant
Final Volume (mls):	10	Department:	ENVSVOCGCMS
Vials:	1	Last Edit:	03/24/09 15:13 by MEF

1ml 9B17007 diluted to 10 ml acetone# 8K11005

Analyte	CAS Number	Concentration	Units
Triclopyr	55336-06-3	100	ug/mL
Picloram	1918-02-1	100	ug/mL
Pentachlorophenol	87-86-5	100	ug/mL
M.C.P.A.	94-74-6	100	ug/mL
Dinoseb	88-85-7	100	ug/mL
Dicamba	1918-00-9	100	ug/mL
Bentazon	25057-89-0	100	ug/mL
2,4-D.B.	94-82-6	100	ug/mL
2,4-D	94-75-7	100	ug/mL
2,4,5-T.P.	93-72-1	100	ug/mL
2,4,5-T	93-76-5	100	ug/mL

Parent Standards used in this standard:

Standard	Description	Prepared	Prepared By	Expires	Last Edit	(mls)
9B17007	MDA List 2 Custom Mix	02/17/09	Mike Frencl	02/12/11	03/24/09 15:13 by MEF	1

Reviewed By   Date

DESCRIPTION:

Sample Preparation for MDA list 1 Pesticides in Solid Sample Matrices using Accelerated Solvent Extraction.

SUMMARY:

This procedure is used to prepare solid samples for the analysis of MDA list 1 pesticides, organo-phosphorus, nitrogen-containing and triazine pesticides. This procedure is based on EPA Method SW-846 3545A. A 30 gram sample is dried using diatomaceous earth and extracted with a 90% methylene chloride and 10% acetone mixture using the Dionex Accelerated Solvent Extractor (ASE) apparatus. The sample extract is concentrated to a 1 mL final volume using the Zymark TurboVap concentration station.

SCOPE:

This procedure complies with the requirements of the Resource Conservation and Recovery Act (RCRA). This SOP is applicable to the preparation of solid samples using accelerated solvent extraction.

DOCUMENT CONTINUITY:

This SOP replaces MDA1SOILPREP Revision 1.

SIGNATURES:

Quality Assurance [signature] Date 5/19/09
Michelle Hubanks

Technical Lead [signature] Date 05/18/2009
Rupali Sawant

Laboratory Manager [signature] Date 05/19/2009
Thomas P. Wagner

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1.0 PERSONNEL QUALIFICATIONS:

1.1 Personnel performing this procedure must be qualified per the requirements outlined in chapter 1 of the Analytical Laboratory Quality Assurance Manual (QAM).

2.0 SAFETY:

2.1 Personnel performing this procedure must follow general laboratory safety practices as defined in chapter 1 of the (QAM).

2.2 When working with organic compounds, wear solvent resistant gloves.

2.3 Follow standard laboratory safety procedures. Always wear a lab coat and safety glasses.

2.4 Review all Material Safety Data Sheets for chemicals used in this procedure.

3.0 DEFINITIONS:

3.1 Refer to standardized Braun Intertec Corporation definitions as described in chapter 4 of the QAM.

3.2 TurboVap tubes: TurboVap 200 mL concentration tubes.

3.3 ASE: Accelerated Solvent Extraction

3.4 $MeCl_2$: Methylene Chloride

3.5 UPDI: Ultra Pure Deionized Water

4.0 FORMS & RECORDS:

4.1 LIMS Bench Sheet, Refer to Appendix A.

4.2 LIMS Standard Record, Refer to Appendix B.

5.0 EQUIPMENT & SUPPLIES:

5.1 Dionex Accelerated Solvent Extractor (ASE) 200.

5.1.1 Stainless Steel Extraction Vessels.

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5.1.2 Filters

5.1.3 Frits

5.1.4 O-rings and gaskets

5.1.5 40 mL vials with PTFE septa caps

5.2 Graduated pipets

5.3 Crimp top vials and PTFE crimp caps

5.4 Zymark TurboVap Concentration Station

5.5 Zymark TurboVap 200 mL Concentration tubes

5.6 Disposable beakers or weigh boats

6.0 REAGENTS & STANDARDS:

6.1 Ultra Pure Deionized Water (UPDI)

6.2 Sodium Sulfate, 10-60 mesh, anhydrous, purified by heating to 450°C for two hours.

6.3 Diatomaceous earth, purified by heating to 450°C for two hours, ICN Biomedicals, Inc (Cat #157606).

6.4 Methylene Chloride, Pesticide grade or equivalent

6.5 Acetone, pesticide grade or equivalent

6.6 Ottawa Sand

6.7 Surrogate Solution – 100 µg/mL of Atrazine-d5 and Diazinon-d10: Prepare surrogate by diluting the appropriate amount of Diazinon-d10 and Atrazine-d5 stock solution to 10 mL final volume of acetone to achieve 100 µg/mL. Record standard preparation in the LIMS.

6.8 Spike Solution – 20 µg/mL of MDA list 1 spike mix: Prepare by diluting 1000 µL of 500 µg/mL MDA List 1 stock standard to a 25 mL final volume of acetone in a

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volumetric flask. Additional analytes may be added as necessary at varying concentrations. Record standard preparation in the LIMS.

7.0 INTERFERENCES & PROCEDURAL LIMITATIONS:

7.1 Rinse all glassware with methylene chloride before use to ensure glassware is clean and free from contaminants.

7.2 Refer to SOP GCMS8270MDAL1 for analytical interferences.

8.0 SAMPLE ACCEPTANCE & HOLDING TIMES:

8.1 Samples must be stored at 4°C from the time of collection to the time of extraction.

8.2 Samples must be extracted within 14 days of sample collection and analyzed within 40 days of extraction.

9.0 CALIBRATION & STANDARDIZATION:

9.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for the calibration and standardization of the GC/MS.

10.0 PROCEDURE:

10.1 Record standard preparation in Element if new standards are needed.

10.1.1 Under Laboratory, click on Standards. Click Add.

10.1.2 For parent standards choose 1. "Specify each analyte and its concentration". Fill in the description, department, expiration date, initials and prepared date. Lot number and additional standard information can be typed in the comment section.

10.1.3 Choose the analytes from the analyte list. To narrow the list, select 8270 MDA List 1 Soils. Select the appropriate compounds from the list and add them to the standard.

10.1.4 Adjust the concentration and the concentration units as necessary.

10.1.5 Make sure the standard type is appropriate (i.e. for spike, click spike. For surrogate, click surrogate).

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10.1.6 To prepare child standards click Add and choose 2. "Combine and/ or dilute existing standards."

10.1.7 Fill in the header information and choose the appropriate parent standard(s). Entering the standard volumes and the final volume will adjust the concentration of the child standard. It will not appear until the standard is saved.

10.1.8 Again, make sure the standard type is appropriate.

10.1.9 For standards that are created new but exactly the same as previous standards instead of choosing add, choose copy. The standard can be copied so that the analytes and concentrations do not need to be added. Fill in the header information with the correct preparation date and expiration date.

10.2 Create a new batch/bench sheet in Element.

10.2.1 Under Laboratory, click Batch. Click Add to create a new batch.

10.2.2 Choose the preparation method, matrix and surrogate. Make sure the surrogate type is pre-prep. In the reagent box, right click and choose the appropriate solvents and reagents used for traceability.

10.2.3 Choose the appropriate analysis and click bench sheet.

10.2.4 On the bench sheet click edit and then add. Choose client samples (by container). Choose all of the samples that will be prepared in that batch. There cannot be more than 20 samples in each batch.

10.2.5 With each batch a MB, BS1, BSD1, MS1, MSD1 will be added. If there is insufficient sample for a MS/MSD pair a sample duplicate can be substituted. To remove QC or samples click on the appropriate sample and choose remove. To add QC click add and choose the appropriate QC sample.

10.2.6 To add information such as initial and final volumes, prepared date, prepared by and comments, highlight samples or QC, right click and choose the appropriate command. Be sure to adjust the sample volume to document the actual sample volume used in extraction.

10.2.7 The LCS/LCSD/MS/MSD standard ID can be added by right clicking on each QC sample and choosing the appropriate command. Also fill in the

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UMP006823

standards type (pre-prep) and the amount spiked. For sample duplicates and MS/MSD the sample source must also be added.

10.2.8 Print the bench sheet using the bch_std06.00.rpt.

10.3 All extraction glassware must be rinsed 3 times with $MeCl_2$ prior to extraction.

10.4 Solvent Rinse ASE extraction vessels with $MeCl_2$. Assemble the stainless steel extraction vessel.

10.4.1 Twist the bottom cap on, the bottom being where the Dionex symbol and a groove are present on the vessel body.

10.4.2 Place a filter into the vessel and push down into the bottom against the cap.

10.5 Prepare samples for extraction.

10.5.1 Weigh approximately 30 grams of each sample into a disposable beaker. Document the actual sample weight on the sample extraction data sheet.

10.5.2 Mix with diatomaceous earth until free flowing to absorb moisture from the sample. In order to achieve optimal recoveries it is extremely important to make sure the sample is completely dry.

10.5.3 For laboratory control samples (LCS/LCSD/MB) use 30 grams of Ottawa sand mixed with diatomaceous earth as the control matrix.

10.5.4 Pour the sample mixed with diatomaceous earth into the vessel on top of the filter.

10.5.5 Deliver 100 µL MDA list 1 surrogate to all samples, including quality control samples.

10.5.6 Deliver 500 µL MDA list 1 spike to the LCS/LCSD and MS/MSD.

10.6 Cap the vessel with the stainless steel cap, and lable the cap with the sample number or QC ID.

10.6.1 Make sure both the top and bottom cap are tight by hand.

10.6.2 If the cap feels loose or rattles, the gasket needs to be changed. The gasket should be changed every 50 runs.

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10.7 Set up the method for the analysis of MDA list 1 samples.

10.7.1 Select BNA only from the schedule for the analysis of MDA list 1 samples. The instrument will default to the parameters in table 1 below.

Table 1: Extraction Parameters	
Parameters	**MDA list 1**
Pressure (psi)	2000
Oven Temperature °C	100
Preheat time (min)	0
Heat Time (min)	5
Static Time (min)	5
Flush Volume (%)	60
Purge Time (sec)	120
Cycles	1

10.7.2 Click the "tray" button on the ASE module to free the turntable. Load the extraction vessels in the labeled slots. Make sure the Dionex symbol on the body is on the bottom side. The filter must be down to filter out particulate from the system.

10.7.3 Put the collection vials in the lower turntable to correspond to the number of vessels in the upper turntable. Don't put the labels on the collection vials before extracting or the instrument will sense that the vial is used and inject the extract into the next vial over.

10.7.4 Make sure the rinse vials are empty and loaded into R1-R4.

10.7.5 Hit the "tray" button again to reengage the turntables. Make sure it lines up with number one.

10.7.6 Once the schedule has been completed and saved, "load" the schedule under File. Press Rinse to flush out the lines and to make sure that there is no air present in the lines. Once the rinse ends, click Run. Check to make sure that the correct schedule appears to be loaded and then the instrument can be allowed to run.

10.8 Collection and concentration of sample extracts.

10.8.1 Once the run is complete, press the tray button again to disengage the turntables. Move the turn table in a position that allows removal of vessels

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and vials. Lable the collection vials with the sample or QC ID from the Turbo Vap vessel caps.

10.8.2 Rinse the appropriate number of TurboVap tubes with methylene chloride.

10.8.3 Label the TurboVap tubes with the appropriate sample ID.

10.8.4 If you notice water present in the extract, add sodium sulfate to the vial to dry the extract. When the sodium sulfate is free flowing the sample is dry.

10.8.5 Pour the sample extracts into the Turbo Vap tubes. Rinse the vails three times with methylene chloride, combining the rinsings into the Turbo Vap tubes. Do not let sodium sulfate to fall into the Turbo Vap tubes.

10.9 Concentrate the extracts down to just below 1 mL in the TurboVap tube. Add $MeCl_2$ drop wise to bring back up to a final volume of 1 mL with a graduated pipet. Quantitatively transfer 1 mL of the extract into a labeled amber autosampler vial and crimp top.

11.0 CALCULATIONS:

11.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for all applicable calculations.

12.0 DATA REDUCTION & RECORDS:

12.1 Once the analysis is complete the GC/MS analyst electronically transfers the data into the LIMS, creates a data packet that includes all applicable forms and raw data and submits data to an authorized technical peer for data verification. Refer to the SOP GCMS8270MDAL1 for more detail.

12.2 All records must be completed at the time of sample preparation. Document all out of the ordinary information on the extraction worksheet such as a sample with a strong odor.

12.3 Extraction paperwork is delivered to the analytical group and the samples are delivered to the GC/MS analyst or stored in the sample preparation laboratory refrigerator freezer door.

13.0 REPORTING:

13.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for information regarding reporting.

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14.0 QUALITY CONTROL:

14.1 Batch QC Frequency:

14.1.1 Batch QC generally consists of a MB, LCS, LCSD, MS and MSD with each set of 20 or fewer samples prepared together.

14.1.2 In situations when insufficient sample is received for MS and MSD a sample duplicate may be substituted for the MSD.

14.1.3 Each sample, including QC samples, is spiked with a surrogate solution to determine extraction efficiency.

14.2 Acceptance Limits for Batch QC:

14.2.1 Please refer to SOP GCMS8270MDAL1 for the batch QC limits.

14.3 Corrective Action for Batch QC:

14.3.1 If the MB, LCS, LCSD or the RPD between the LCS and LCSD are outside of acceptance limits then the batch must be re-extracted and reanalyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

14.3.2 If the MS/MSD, including the RPD between the MS/MSD is outside the acceptance limits then the data associated with the project from which that MS/MSD originated must be appropriately qualified. This assumes that the QC in 14.3.1 is within acceptance limits. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

14.3.3 If the sample surrogates are outside of acceptance limits the specific sample must be re-extracted and re-analyzed, provided sample is available. If sample is not available then the associated data must be qualified. If any of the QC is outside of acceptance limits, follow the current non-conformance procedure as is outlined in the QAM.

15.0 METHOD PERFORMANCE:

15.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for all applicable method performance.

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16.0 DETECTION LIMITS:

16.1 Not applicable to the sample preparation SOP. Refer to SOP GCMS8270MDAL1 for all applicable detection and reporting limits.

17.0 REFERENCES:

17.1 PRIMARY REFERENCES:

17.1.1 US EPA SW-846 Method 3545

17.2 SECONDARY REFERENCES:

17.2.1 Dionex AutoASE Software Users Guide, 1997 Dionex Corporation

18.0 WASTE MANAGEMENT & POLLUTION PREVENTION:

18.1 Please refer to the general policies and procedures outlined in chapter 7 of the QAM regarding waste management and pollution prevention.

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Appendix A

Preparation Bench Sheet

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PREPARATION BENCH SHEET

B8J0694

Braun Intertec Corporation

Analysis: List 1 Soil

Logbook:

Matrix: Soil

Analyst: LET

Printed: 5/7/2009 9:44:20AM

Prepared using: ENVSVOCGCMS - EPA 3545

Surrogate ID: 8J29044

Lab Number	Prepared	Initial (g)	Final (mL)	Spike ID	uL Spike	Source ID	uL Surrogate	Position	Extraction Comments
0806615-01	10/30/08 09:13	30.41	1				100		
0806615-02	10/30/08 09:13	30.88	1				100		
0806615-05	10/30/08 09:13	30.21	1				100		
0806615-06	10/30/08 09:13	30.64	1				100		
0806615-07	10/30/08 09:13	30.46	1				100		
0806615-08	10/30/08 09:13	30.09	1				100		
0806615-09	10/30/08 09:13	30	1				100		
0806615-09RE1	10/30/08 09:13	30	1				100		Re-extract added 11/4/2008 by MEF
0806615-10	10/30/08 09:13	30.42	1				100		
0806615-11	10/30/08 09:13	30.53	1				100		
0806615-14	10/30/08 09:13	30.74	1				100		
0806615-15	10/30/08 09:13	30.2	1				100		
0806615-17	10/30/08 09:13	30.35	1				100		
0806615-20	10/30/08 09:13	30.1	1				100		
0806615-21	10/30/08 09:13	30.17	1				100		
0806615-37	10/30/08 09:13	30.27	1				100		
B8J0694-BLK1	10/30/08 09:13	30.14	1				100		
B8J0694-BS1	10/30/08 09:13	30.04	1	8J29045	500		100		
B8J0694-BSD1	10/30/08 09:13	30.05	1	8J29045	500		100		
B8J0694-MS1	10/30/08 09:13	30.09	1	8J29045	500	0806615-08	100		
B8J0694-MSD1	10/30/08 09:13	30.28	1	8J29045	500	0806615-08	100		

PREPARATION BENCH SHEET

B8J0694

Braun Intertec Corporation

Analysis: List 1 Soil
Logbook:
Matrix: Soil

Analyst: LET
Printed: 5/7/2009 9:44:20AM

Prepared using: ENVSVOCGCMS - EPA 3545

Surrogate ID: 8J29044

Lab Number	Prepared	Initial (g)	Final (mL)	Spike ID	uL Spike	Source ID	uL Surrogate	Position	Extraction Comments

Reagent	Description
8H07002	Diatomaceous Earth
8H14004	Sodium Sulfate
8H22033	Ottawa Sand
8I29042	Acetone Pesticide Grade
8J24001	Methylene Chloride
8J29044	MDA List 1 Surrogate 100 ug/mL
8J29045	MDA L1 SPIKE SOLN, 20ug/ml

Appendix B

Analytical Standard Record

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UMP006832

Analytical Standard Record

Braun Intertec Corporation

9D15016

Description:	MDA List 1 Surrogate 100 ug/mL	Expires:	10/12/09
Standard Type:	Surrogate Spike	Prepared:	04/15/09
Solvent:	8K11005	Prepared By:	Rupali Sawant
Final Volume (mls):	5	Department:	ENVSVOCGCMS
Vials:	1	Last Edit:	04/15/09 09:06 by RSS

1 ml stock diluted to 5ml with acetone

Analyte	CAS Number	Concentration	Units
Diazinon-d10		100	ug/mL
Atrazine-d5		100	ug/mL

Parent Standards used in this standard:

Standard	Description	Prepared	Prepared By	Expires	Last Edit	(mls)
8I25039	MDA L1 Surrogate Stock (500ug/n	09/25/08	** Vendor **	01/01/10	09/25/08 12:03 by NPL	1

Reviewed By ______________________ Date

UMR006833

Title: Determination of Perchlorate by Ion Chromatography

[Method 314.0]

Approvals (Signature/Date):

4/9/09		4/10/09	
David Allameh Technical Manager	Date	Joe Schairer Health & Safety Manager / Coordinator	Date
04/13/09		4/15/09	
Douglas Weir Quality Assurance Manager	Date	Karla Buechler Laboratory Director	Date

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1. SCOPE AND APPLICATION

1.1. This procedure is based on EPA Method 314.0, Revision 1.0, November 1999, Dionex Application Note 134, Dionex Application Note 145, and Dionex IonPac AS16 Anion-Exchange Column Literature.

1.2. This method covers the determination of perchlorate in drinking, ground, and surface waters using ion chromatography. Soils and wastes may also be analyzed using this procedure, following a DI Leach preparation according to SOP number WS-WC-0049.

1.3. This method is only for use by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.4. This SOP specifies the use of a Dionex AG16, 4 mm guard column and an AS16, 4 mm analytical column, and analytical conditions to meet method specifications. Equivalent columns or conditions may be used if method requirements are still met.

1.5. The reporting limit is 4.0 ug/L for aqueous samples and 40 ug/kg for solid samples. Lower reporting limits are achievable and may be implemented on a client or project specific basis.

2. SUMMARY OF METHOD

2.1. A 1.0 mL volume of sample is introduced into an ion chromatograph (IC). Perchlorate is separated and measured, using a system comprised of an ion chromatographic pump, sample injection valve, guard column, analytical column, suppressor device, and conductivity detector.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Manual (QAM).

3.2. Data qualifiers are defined on each data report. Commonly used data qualifiers are defined in the QAM.

4. INTERFERENCES

4.1. 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 an ion chromatogram. These interferences can lead to false positive results for the target analyte as well as reduced detection limits as a consequence of elevated baseline noise.

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4.2. Samples and reagent solutions that contain particulates larger than 0.45 microns require filtration to prevent damage to instrument columns and flow systems. Particulates can be separated by filtering the samples, standards, or reagents through a filter syringe with a 0.45 micron filter cartridge. All samples and standards pass through filter caps prior to injection. This filtering is sufficient when small amounts of particulate are present in a sample.

4.3. Sample matrices with high concentrations of common anions such as chloride, sulfate, and carbonate can destabilize the baseline in the perchlorate retention time window. This is evidenced by observing a protracted trailing following these anions, extending into the perchlorate window. These anions can be detected by conductivity testing, and dilutions should be performed accordingly.

4.4. A noisy baseline will also interfere with accurate recovery. Baseline noise is considered unacceptable if the peak noise listed on the summary sheet for the rinse is greater than 0.005. If the instrument sits idle for more than a week or runs out of eluent or external water, the suppressor can become dry or overheated and will be unable to produce a clean baseline. Air bubbles trapped in the system, particularly in the pump or conductivity cell, can also cause a noisy baseline.

4.4.1. See the instrument manual for specific instructions on priming the pump, regenerating the suppressor, and flushing the conductivity cell.

4.5. Over time, some matrices will affect suppressor performance. This is evidenced by reduced peak response or asymmetrical perchlorate peaks, and should be corrected by cleaning the suppressor membranes according to manufacturer's instructions.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the West Sacramento Addendum to the Corporate EH&S Manual (WS-PEHS-002) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toed, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

5.1.1. 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.

5.1.2. Eye protection that satisfies ANSI Z87.1, laboratory coat, and chemically

resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. PVC, latex and nitrile gloves provide adequate levels of protection against the chemicals used in this SOP.

5.1.3. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore all samples must be opened, transferred and prepared in a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.1.4. Laboratory procedures such as repetitive use of pipets, repetitive transferring of extracts, and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

5.2. Primary Materials Used

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
Potassium Hydroxide	Corrosive	Undetermined	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 Perchlorate	Oxidizer	None Listed	Strong oxidizer. Contact with other material may cause a fire. Contact may cause severe eye, skin and respiratory tract irritation with possible burns.
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. Ion Chromatograph (IC) – This method uses IC instrumentation manufactured by Dionex, Model ICS2000. Equipped with an autosampler, injection valve, pump with 1.5 mL/min flow rate, integrator, 1 mL sample loop, eluent generator, data acquisition system, and set up with the following components:

6.1.1. Columns: Dionex AG16, 4 mm (P/N 055377) and Dionex AS16, 4 mm (P/N 055376).

6.1.2. Suppressor: Dionex ASRS ULTRA II (P/N 061561), external water mode, 200 mA current.

6.1.3. Potassium Hydroxide EluGen Cartridge (P/N 058900)

6.2. Balance – Analytical balance capable of accurately weighing to the nearest 0.0001 g.

6.3. Syringe, disposable, 2-10 mL capacity and equipped with male pressure fitting.

6.4. 0.45 micron acrodisc filters.

6.5. Dionex IC sample vials and filter caps –at least 5 mL capacity (P/N 38141).

6.6. Various Class A analytical glassware of different sizes – graduated cylinders, volumetric flasks, pipettes, etc.

6.7. Plastic bottles – 2-4 L bottles are ideal for water and eluent reservoirs.

6.8. Conductivity meter

Note: It is permissible to change columns types, injection volumes, and/or eluents to improve separation or to lower costs, provided that the initial demonstration of capability is repeated and that the specifications as detailed in the reference EPA Method 314.0 are met.

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 the 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 anions of interest. Water should contain particles no larger than 0.20 micron and have a resistance of at least 18 mega-

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ohms. For best results, use reagent water that is taken directly from the Nanopure water system.

7.3. Eluent solution: Eluent is made by the eluent generator in the KOH EluGen Cartridge that is fed by a 2 L poly bottle of degassed nanopure. For normal operation the eluent generator is set to produce 50 mM KOH eluent.

7.4. Perchlorate stock solution, 1000 mg/L (or 1,000,000 ug/L): Obtain commercially. Alternatively, use a 1000 mL volumetric flask filled with approximately 600 mL of reagent water. Dissolve 1.2314 grams of sodium perchlorate (99% purity). (Note: sodium perchlorate represents a molar weight fraction of 81.2% perchlorate anion). Dilute to the mark with reagent water. Good for one year.

7.4.1. Intermediate standard solution, 10 mg/L (or 10,000 ug/L): Using a 100 mL volumetric flask containing at least 50 mL of reagent water, pipette 1 mL of the 1000 mg/L stock solution and swirl gently. Dilute to the mark with reagent water. Good for one month.

7.4.2. Working standards: Linear range 1 ug/L to 100 ug/L, good for one month. Dilute the intermediate standard (10,000 ug/L) with reagent water into volumetric flasks as follows:

Standard #	Aliquot (mL)	Final Volume (mL)	Final concentration (ug/L)
1	0.05	500	1.0
2	0.08	200	4.0
3	0.2	100	20
4	0.8	200	40
5	3.0	500	60
6	0.8	100	80
7	5.0	500	100

7.5. Second-Source Stock Standard, 100 mg/L (or 100,000ug/L): Obtain commercially. Alternatively, the second-source standard can be prepared from a different lot or different manufacturer other than the source of the Calibration Stock Standard. Good for 1 year.

7.6. Second-Source Working Standard:

7.6.1. 50 ug/L: Dilute 0.1 mL of the second-source stock standard to 200 mL in a volumetric flask for a final concentration of 50 ug/L. Good for one month.

7.7. Mixed Anion Stock Solution: Dissolve the following salts in reagent water for a final volume of 100 mL: 4.0 grams NaCl, 3.7 grams Na_2SO_4, and 4.4 grams Na_2CO_3. Final concentration: 25,000 mg/L chloride, sulfate, and carbonate anions. Good for one year.

7.8. Maximum Conductivity Threshold Standard (MCT) or Initial Performance Check standard (IPC), 25 ug/L perchlorate and 200 ug/L mixed anion standard: Mix 0.5 mL of the 10,000 ug/L perchlorate stock solution with 1.6 mL mixed anion stock solution to a final volume of 200 mL. Good for one month.

Note: The MCT level can be adjusted, provided that the procedure in reference EPA Method 314.0 is followed.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples should be collected in pre-cleaned plastic or glass containers. The volume collected should be sufficient to ensure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

8.2. Samples are stored at room temperature, no preservative.

8.3. Samples should be analyzed within 28 days of collection.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability: All analysts must successfully complete 4 laboratory control samples (LCS) prior to the analysis of any samples. Calculate the average recovery and standard deviation of the recovery. If the analyte does not meet the acceptance criteria, the test must be repeated. Repeated failure of the test indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

9.2. Method Detection Limit (MDL): The MDL is determined as described in SOP WS-QA-0006, "MDLs and IDLs", and CA-Q-S-006, "Detection Limits". The study must be carried out over the course of a three day period in accordance with EPA method 314.0. An alternative to running the MDL study annually, an MDL check standard may be run quarterly to verify the existing MDL.

9.3. Maximum Conductivity Threshold (MCT): The highest permitted conductance of an unknown sample matrix, measured prior to conducting the analysis, which is used to determine when sample matrix dilution is required. The conductance in the MCT/sample is proportional to the concentration of common anions present. The MCT and the Instrument Performance Check (IPC) contain perchlorate, as well as the common anions of chloride, sulfate, and carbonate. These common anions are known to elute into the perchlorate window and cause potential interference. An MCT study will be performed annually. After the MCT is determined, it must be confirmed in each batch by the IPC. The IPC must meet three criteria:

9.3.1. Percent Difference of Area/Height ratio between the ICV and the IPC solution $< 25\%$.

9.3.2. 80%-120% Perchlorate Recovery.

9.3.3. Retention time shift < 5% from ICV.

9.3.4. Corrective action: Restart batch. If the IPC fails repeatedly, the MCT must be re-established.

9.4. Minimum Reporting Level (MRL) - The MRL is the threshold concentration of an analyte that a laboratory can expect to accurately quantitative in a sample. An MRL verification set at the MCT will be run annually.

9.5. Batch: A quality control batch is a set of up to 20 field samples that have the same matrix and are processed using the same procedures, reagents, and standards within a 30 hour time period. A method blank (MB), LCS and matrix spike/matrix spike duplicate (MS/MSD) are also part of the batch. An analysis batch must also include all QC samples, however they do not contribute to the maximum of 20 samples.

Note: A field sample from the original batch can be reanalyzed after the closing CCV/CCB if it is still within 30 hours of the start of the run. An ICCS, as well as a CCV/CCB must be analyzed first, and the run must close with another CCV/CCB within that 30-hour window.

9.6. One Method Blank (MB) must be processed with every batch of similar matrix, not to exceed twenty (20) samples. The method blank is an aliquot of laboratory reagent water processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, as described in SOP WS-QA-0023, then implemented when target analytes are detected in the method blank above the reporting limit. Re-extraction of the blank, other batch QC and the affected samples are required when the method blank is deemed unacceptable.

9.6.1. For aqueous analyses, the ICB is evaluated as the MB.

9.6.2. For solid analyses, a blank is prepared with the batch.

9.7. A Laboratory Control Sample (LCS) must be processed with every batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. water, Ottawa sand, sodium sulfate, etc.) spiked with analytes of known identity and concentration. The LCS must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented in a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside control limits provided in a Laboratory Information Management System (LIMS) or by the client. Re-extraction of the blank, other batch QC, and all associated samples are required if the LCS is deemed unacceptable. Refer to the Quality Program document, WS-PQA-0003, for specific acceptance criteria.

9.7.1. For aqueous analyses, the ICV is evaluated as the LCS.

9.7.2. Solid LCS are spiked with a concentration of 500 ug/kg. A blank is prepared with the batch and spiked just prior to analysis.

9.7.3. LCS/LCSD recoveries must meet 85-115 % criteria, however, if the ICV is evaluated as the LCS/LCSD it must also meet 90-110% criteria with an RPD of < 15% for aqueous samples, and 75 – 125% with an RPD of < 20% for solid matrices.

9.8. A Matrix Spike/Matrix Spike Duplicate (MS/MSD or MS/SD) pair must be processed with every batch of similar matrix, not to exceed twenty (20) samples. MS/MSD are aliquots of a selected field sample spiked with analytes of known identity and concentration. The MS/MSD pair must be processed in the same manner and at the same time as the associated samples. Spiked analytes with recoveries or precision outside control limits must be within control limits for the LCS. Corrective actions must be documented in a Non-Conformance memo, then implemented when recoveries of any spike analyte is outside control limits provided in LIMS or by the client. Re-extraction of the blank, LCS, the selected field sample and the MS/MSD may be required after evaluation and review.

9.8.1. Two aliquots of an aqueous sample are spiked with a concentration of 50 ug/L.

9.8.2. Solid samples are spiked with a concentration of 500 ug/kg. A sample duplicate is prepared with the batch and two aliquots are spiked just prior to analysis.

9.8.3. MS/SD recoveries must be 80 – 120% with an RPD of < 20 for aqueous, and 75 – 125% with an RPD of < 20% for solid matrices.

9.9. A duplicate control sample (LCSD or DCS) may be substituted when insufficient sample volume is provided to process an MS/MSD pair or as required by state or client requirements. The LCSD is evaluated in the same manner as the LCS. Refer to the Quality Program document, WS-PQA-003, for specific acceptance criteria.

9.9.1. For aqueous samples, an additional ICV standard can be analyzed, or two CCVs of identical concentration can be evaluated as the LCS/DCS.

9.10. The QC terms and criteria listed below are a combination of those specified by EPA Method 314.0 and TestAmerica West Sacramento standard QC requirements.

Acceptance Criteria and Corrective Actions-Perchlorate			
QC Type	***Frequency***	***Acceptance Criteria***	***Corrective Action***
Initial Calibration Curve	Calibrated initially, then monthly. Verified daily prior to analysis.	r > 0.995	Reanalyze once. If the problem persists, reprepare the standards, and recalibrate. If the problem persists, consult the supervisor for instrument repair.

Acceptance Criteria and Corrective Actions-Perchlorate			
QC Type	***Frequency***	***Acceptance Criteria***	***Corrective Action***
ICV-50ppb (Second Source Standard)	At start of every analytical sequence, following the initial calibration.	90%-110% Recovery	Reanalyze once. If the problem persists, reprepare the standards, reanalyze, and/or recalibrate.
REF/LCS-50ppb (Second Source Standard)	At start of every analytical sequence, following the initial calibration.	85%-115% Recovery	Reanalyze once. If the problem persists, reprepare the standards, reanalyze, and/or recalibrate.
ICB/CCB/MB	Directly following ICV/CCVs.	<1/2 Reporting Limit	Reanalyze once. If the problem persists, isolate the source of the problem and fix it. If the problem is isolated to the blank, reprepare, reanalyze and proceed. If the problem may have affected previous sample results (i.e. instrument failure, contaminated vials, etc.), reanalyze samples bracketed by the failed blank.
IPC/MCT-25ppb perchlorate, 200 ppm anions	1 per batch of 20 samples or fewer. Annual(MCT study)	1. Percent Difference of Area/Height ratio between the ICV and the MCT solution <25% 2. 80%-120% Perchlorate Recovery 3. Retention time shift <5%	Restart analysis. If problem persists, MCT level may need to be reestablished. Annual study see Method 314.0 section 9.2.8
MRL-4ppb (or 1 ppb)	Annual	Prepared within ±10% of the MCT. Perchlorate recovery must be 70-130% of the MRL	Reanalyze once. If the problem persists, reprepare the standards, reanalyze, and/or recalibrate.
ICCS-4ppb	At start of every analytical sequence, following the MCT.	75%-125% Recovery	Restart analysis. If baseline is noisy, attempt to reduce baseline noise. Recalibration may be necessary.
CCV-Alternate 60ppb/100ppb	After every 10 samples and at the end of the analytical sequence.	85%-115% Recovery	Reanalyze once. If the problem persists, isolate the source of the problem and fix it. If the problem is isolated to the standard (i.e. misspike, etc.), reprepare, reanalyze and proceed. If the problem may have affected previous sample results (i.e. instrument failure, contaminated vials, etc.), reanalyze samples bracketed by the failed standard.
MS/SD-50ppb aqueous -500ppb solid	1 MS/MSD pair per batch of 20 samples or fewer.	Aqueous: 80%-120% Recovery, 15%RPD Solid: 75%-125% Recovery, 20%RPD	Reanalyze once. If reanalysis recovery fails but % RPD passes, accept data. If reanalysis passes, report reanalysis.
MB-solid (ICB=MB for aqueous)	1 per batch of 20 samples or fewer	< Reporting limit	Reanalyze once. If problem persists, reprepare and reanalyze batch.
LCS - solid (ICV=LCS for aqueous)	1 per batch of 20 samples or fewer	75%-125%	Respike aliquot and reanalyze. If problem persists, reprepare and reanalyze batch.

Acceptance Criteria and Corrective Actions-Perchlorate			
QC Type	***Frequency***	***Acceptance Criteria***	***Corrective Action***
Samples: (Conductivity of the sample must be measured and recorded prior to analysis).	Water-no preservative. Soil-10X 1 hour DI leach. 28 day hold time.	RLw=4ppb, 1ppb RLs=40ppb	Conductivity of the water aliquot must be less than the conductivity of the MCT/IPC. If higher, dilute prior to analysis.

10. CALIBRATION

10.1. Initial Instrument Calibration (ICAL): A minimum of five calibration standards that represent the linear range of the instrument are analyzed and used as the instrument calibration for a month. The initial calibration sequence is listed below:

Reagent Water
1 ppb Standard
4 ppb Standard
20 ppb Standard
40 ppb Standard
60 ppb Standard
80 ppb Standard
100 ppb Standard

10.1.1. Frequency: Initially, then monthly, or as required due to failed ICV/CCV. Verify daily with an ICV.

10.1.2. Criteria: r value of 0.995 or better.

10.1.3. Corrective Action for failed ICAL: Recalibrate. If ICAL fails again, check standards and remake as needed. For failed linear curve due to instrument failure, consult a Dionex service representative.

10.1.4. Retention time of samples and standards should be within 5% of that obtained during the initial calibration. If a shift of > 5% occurs, results can be used after filing an NCM, provided that the shift is confirmed by the daily QC. The instrument should be recalibrated prior to initiating a new analysis.

NOTE: A reagent water blank is analyzed prior to the instrument calibration in order to verify that the instrument baseline is stable and peak to peak criteria is met. The peak noise must be less than 0.005.

11. PROCEDURE

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. Instrument Start-up: Ensure that all start-up procedures and instrument parameters are documented in the daily maintenance logbook.

11.2.1. Check the waste carboy to make sure there is enough room for the run to continue without any overflow.

11.2.2. Use fresh nanopure water that has been degassed with nitrogen or helium to fill the eluent generator feed bottle, and fill the external rinse bottle with nanopure.

11.2.3. Hit the "Start" button on the Chromeleon software control panel. Set the flow rate to 1.5 mL/min, eluent generator to 50 mM, and the suppressor current to 200 mA.

11.2.4. Check the system and pumps for any leaks and repair if needed.

11.2.5. Once the system has stabilized, a constant pressure should be reached. If pressure is unstable, stop the system and prime the pump following instrument recommended procedures. If pressure continues to fluctuate, the pump will need to be taken apart and the seals replaced.

11.2.6. Ensure that external water is flowing through the suppressor. A steady flow of water and gas bubbles should be seen flowing out of the suppressor. When replacing the suppressor the flow rate may need to be adjusted at the start of each run until it has a constant flow rate of 3-4 mL/min.

11.2.7. Check system pressure: Normal operating pressure for this system is 2200-2800 psi. The system is also equipped with an auto-shutoff if the pressure exceeds 3000 psi to ensure the instrument is not damaged. It is normal for the system pressure to increase during the life of the columns. Periodically it will be necessary to replace the filter frits on the inlet side of the columns to reduce this pressure.

11.2.8. As soon as the backpressure is stable around 2400 psi, baseline total uS is < 2 uS and the pk to pk noise is < 0.015, the instrument is ready for analysis.

11.3. Sample Pretreatment

11.3.1. Measure the conductivity of the sample using a calibrated conductivity meter

and record the readings in the appropriate instrument logbook. If the conductivity of the sample is greater than the conductivity of the MCT/IPC, dilute the sample prior to analysis. Measure and record the conductivity of the diluted sample. The sample must be diluted to the point that the conductivity of the sample or diluted portion thereof is less than the conductivity of the MCT/IPC. The reporting limit associated with the diluted sample will increase in proportion to the dilution.

11.3.2. Filter colored or turbid samples prior to analysis.

11.3.3. Arrange standard and sample vials in the same order as below. Two reagent water blanks are recommended prior to each analytical run to confirm a stable baseline.

ICV	@ 50 ppb, (use as aqueous LCS)
ICB	
IPC (MCT)	@ 25 ppb, with 500 ppb mixed anions.
ICCS	@ 4 ppb or 1 ppb
10 samples, including QC below	
LCS	@ 500 ppb (soils only)
MS	@ 10 ppb (waters), 500 ppb (soils)
MSD	@ 10 ppb (waters), 500 ppb (soils)
CCV	@ 60 ppb
CCB	
10 samples	
CCV	@ 100 ppb
CCB	

11.4. Sample Analysis

11.4.1. Build analysis schedule as noted above.

11.4.2. On the autosampler, make sure it is in the "Run" mode.

11.4.3. Under the batch control tab select start, or press the "play" button.

11.4.4. Occasionally, monitor run and noise level.

11.4.5. Monitor water and eluent levels while the run is in progress.

11.5. Instrument Shutdown

11.5.1. Using the control panel, press the "stop" button. This will stop the pump, turn

off the suppressor current, and stop the external water flow.

-OR-

11.5.2. In the last line of the schedule, enter shutdown as the program.

11.6. Standard Conditions and Equipment

Parameter	Setting
Ion Chromatograph	Dionex ICS 2000
Sample Loop	1 mL
Eluent	50.0 mM KOH
Eluent Flow	1.5 mL/min
Columns	Dionex AG-16 4mm / AS16 4mm
Suppressor	ASRS Ultra II, external mode, 200 mA current
Peak Noise	< 0.005
Background Conductivity	< 2 uS
Typical System Backpressure	2200 psi – 2800 psi
Approximate Retention Time	8.5 – 9.5 minutes
Allowable RT shift between calibrations	5%
Approximate Analysis Time	15 minutes

12. CALCULATIONS/DATA REDUCTION

12.1. Perchlorate Identification

12.1.1. Identification occurs when a peak matching the retention time of the reference standard is found at a concentration above the reporting limit, or above the MDL if J flags are required.

12.1.2. If the analyst is unsure of perchlorate in the sample due to matrix, retention time shifts, or other factors, the sample should be spiked, analyzed and evaluated. A split or shouldering peak is evidence of an interferent and should not be reported as perchlorate.

12.1.3. The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in a variance of retention times.

12.1.4. All manual or re-integration of chromatograms must be documented in accordance with Policy CA-Q-S-002 and the West Sacramento-specific addendum. Documentation includes, as a minimum, before and after copies of the chromatograms with a reference to the reason for re-integration, and analyst's and reviewer's initials and the date on the re-integration.

12.2. Calibration Range

12.2.1. If the concentration of the perchlorate anion exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. The reporting limit must be raised accordingly.

12.2.2. Responses for the diluted sample must be at a minimum 3-5 times the level of the lowest standard.

12.2.3. It may be necessary to dilute samples due to matrix.

12.3. Calculations

12.3.1. Peak areas are used as a measure of response since they have been found to be more consistent than peak heights.

12.3.2. All sample concentrations are calculated based on a quadratic equation. The calculation is automatically performed by the instrument, based on the equation:

Equation 1 Concentration = $Ax^2 + Bx + C$

Where: A = 2nd order coefficient

B = 1st order coefficient

C = constant

Equation 2 Conc in Sample (ug/L) = Concentration (ug/L) x DF

Where: DF = Dilution Factor

Equation 3 Conc in Sample (ug/kg) = Concentration (ug/L) x (V_l/M_s) x DF

Where: DF = Dilution Factor

V_l = Volume of Leachate (in L)

M_s = Mass of soil (in kg)

12.4. Reporting Requirements

12.4.1. When it is necessary to redraw baselines, the redraw must be saved in the data system and both the original and redraw included in the data pack.

12.4.2. Reporting limits and units are described in Section 1.5.

12.4.3. Sample results are entered into a LIMS system in accordance with current QA policies.

12.4.4. Footnotes and anomalies when applicable must be included in the data pack

and data reduction process. Exceeded holding times must be immediately communicated to the project managers and followed by an electronically filed non-conformance memo.

13. METHOD PERFORMANCE

13.1. 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 expertise.

13.2. Method Detection Limit

The laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in SOP WS-QA-0006. MDLs are available in the Quality Assurance Department.

13.2.1. The study must be carried out over the course of a three day period in accordance with EPA Method 314.0. In addition, instead of running the MDL annually, an MDL check standard may be run quarterly to verify the existing MDL.

13.3. Initial Demonstration

The laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.3.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be less than or equivalent to the LCS samples.

13.3.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these to the laboratory generated QC Limits.

13.4. If any analyte does not meet the acceptance criteria the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.5. The laboratory must run the MCT study and must confirm the perchlorate MRL annually. See section 9.2.8 from EPA Method 314.0, Determination of Perchlorate in Drinking Water using Ion Chromatography, Revision 1.0, November 1999.

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14. POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15. WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP WS-EHS-0001. The following waste streams are produced when this method is carried out.

15.1. Assorted test tubes, autovials, syringes and filter discs. Dump the solid waste into a contaminated lab trash bucket. When the bucket is full or at the end of the day, tie the plastic bag liner shut and put the lab trash into the steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.2. Unused sample material. Pour any excess liquid into a 1-liter to 4-liter HPLC collection carboy at the fume hood. When the carboy is full, or at the end of your shift, whichever comes first, empty the carboy into the plastic HPLC collection drum in the H3 closet. When the drum is full to between one and four inches from the top, or after no more than 75 days, move the drum to the waste collection area for shipment.

15.3. Eluent waste from the analytical process. The waste from the instrument is collected in 5 gallon carboys. When full, or after no more than one year, transfer the full jug to the main waste area for shipment.

16. REFERENCES/CROSS REFERENCES

16.1. EPA Method 314.0, Determination of Perchlorate in Drinking Water using Ion Chromatography, Revision 1.0, November 1999.

16.2. Dionex Application Note 134.

16.3. Dionex IonPac AS16 Anion – Exchange Column Literature.

16.4. WS-QA-0041 Calibration and Calibration Check of Balances.

16.5. WS-PQA-008 Data Recording Requirements.

16.6. WS-PQA-0003 Quality Control Program

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16.7. WS-WC-0009 Determination of Anions by Ion Chromatography

16.8. WS-WC-0049 Deionized Leaching Procedure for General Chemistry Analyses.

16.9. WS-QA-0023, Nonconformance and Corrective Action System

16.10. WS-QA-0006, Method Detection Limits and Instrument Detection Limits

17. METHOD MODIFICATIONS

17.1. Alternate matrices included.

18. ATTACHMENTS

18.1. None.

19. REVISION HISTORY

19.1. WS-WC-0010, Revision 4, Effective 04/17/2009

19.1.1. Updated to TestAmerica format.

19.1.2. Removed high-level curve.

19.1.3. Editorial changes.

19.1.4. Removed reference to high-level/low-level curve, consolidated to a single calibration curve.

19.1.5. Fixed the units for the MCT standard.

19.1.6. Updated the calculations to reflect the quadratic regression currently in use.

19.2. SAC-WC-0010, Revision 3, Effective 7/27/2007

19.2.1. The reporting limit was lowered to 1 ug/L and 4 ug/L for aqueous samples and 40 mg/kg for soil samples. The units were also corrected to read in ug instead of mg.

19.2.2. The linear range was changed to 1 ug/L-100 ug/L.

19.2.3. MDL study updated to follow method requirement of being carried out over a three day period.

19.2.4. New instrument procedures for ICS2000 added.

19.3. SAC-WC-0010, Revision 2, Effective 03/04/2003

19.3.1. The reporting limit was lowered to 4 ug/L for aqueous samples and 40 mg/kg for soil samples. The units were also corrected to read in ug instead of mg.

19.3.2. The MDL check standard was removed, as it was an extra step that was not required by the method or STL's MDL policy.

19.3.3. The sample duplicate was also removed. Per the method, it is necessary to run a sample duplicate, an LCSD, or an MSD per batch for precision monitoring. This requirement is met with the MSD.

19.3.4. Stock standards are to be obtained commercially rather than made from salts when possible.

19.3.5. The linear range was changed to 2 ug/L-100 ug/L.

19.3.6. Additional acceptance criteria for the IPC were added to reflect method requirements.

19.3.7. The level of the MCT was updated.

Title: Preparation and Analysis of Nitrocellulose in Aqueous and Soil/Sediment Samples by Colorimetric AutoAnalyzer [Method 353.2]

Approvals (Signature/Date):

Jeff Rogers, Technical Manager — Date: 4.22.09	Joe Schairer, Health & Safety Manager / Coordinator — Date: 4/22/09
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1. SCOPE AND APPLICATION

1.1. This method determines nitrocellulose (NC, CAS Number 9004-70-0) by calculation from detected nitrate and nitrite concentrations in aqueous and soil/sediment samples.

1.2. The analytical range for this method is 0.050 to 2.0 mg/L for nitrate plus nitrite. Samples that are over the linear range are diluted and reanalyzed.

1.3. The QuanTIMs method code is WA; cross-reference NCEL_[A, S].

2. SUMMARY OF METHOD

2.1. Nitrocellulose is extracted by filtering an aqueous sample through a membrane filter. The membrane filter is extracted with acetone, which is collected in a 50 mL tube.

2.2. Soil/sediment samples for nitrocellulose are washed two times with 1:1 methanol-water. Following the rinse, the soil residue is extracted with acetone, which is decanted into a 50 mL tube.

2.3. The acetone extracts are mixed with sodium hydroxide, and reduced under nitrogen until the acetone has evaporated. The basic solution is heated to hydrolyze the NC to nitrate/nitrite, and then brought up to volume with water. After pH adjustment, an aliquot is filtered and analyzed colorimetrically for nitrate plus nitrite by method MCAWW 353.2.

2.4. Extracts are analyzed on an automated colorimetry instrument fitted with a cadmium reduction coil. A filtered sample is passed through a reduction column to reduce nitrate to nitrite. The sample is then treated to form a highly colored azo dye that is measured colorimetrically. The absorbance is directly proportional to the concentration of nitrate plus nitrite as N.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Manual (QAM).

3.2. Data qualifiers are defined on each data report. Commonly used data qualifiers are defined in the QAM.

4. INTERFERENCES

4.1. Nitrocellulose, nitroaromatics and nitroamines cannot be differentiated from each other by this method.

UMP006854

4.1.1. Nitroaromatics and nitroamines may be removed from the soil/sediment by washing with 1:1 methanol-water before extraction.

4.2. Build up of suspended matter in the column restricts sample flow. Particulates are removed by filtering the samples using 0.45 μm filters.

4.3. Iron, copper, and other metals may interfere with the accurate analysis of nitrate and nitrite by binding with the nitrate and/or nitrite in the sample, thus blocking the color formation reaction. EDTA is used in the buffer solution to eliminate the interference.

4.4. Oil and grease will coat the cadmium surface and cause low recoveries. This interference can be removed from the samples by pre-extraction with an organic solvent such as chloroform, methylene chloride, or another suitable solvent.

4.5. Samples preserved with mercuric chloride or sodium thiosulfate will degrade the cadmium reduction column. DO NOT analyze such samples by this method.

4.6. Physical interferences such as color and turbidity in the samples will cause high results and can be minimized by filtration or dilution.

4.7. Samples that discolor when exposed to air for an extended period of time must be analyzed immediately. For this type of sample, it is recommended to pour the solution into the sample cup immediately prior to sample injection to minimize exposure to air.

4.8. Contaminants in solvents, reagents, glassware, and other processing hardware can cause interferences that lead to discrete artifacts and an elevated baseline in the analysis. These materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks and/or method blanks.

4.8.1. Reagent blanks and/or method blanks are analyzed with each batch to demonstrate that the samples are free from method interferences and artifacts.

4.9. The standards and reagents used should be the highest grade possible to minimize interference problems, minimally reagent grade.

5. SAFETY

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual, Local Supplement to the EHSM, and this document.

5.1. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

5.1.1. Handle nitrocellulose (NC) with care, especially when the nitrocellulose contains a high percentage of nitrogen (10% to 14% N). NC is unstable and explosive when dried.

5.1.2. 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.

5.1.3. The use of vacuum systems during Anodisc membrane filtering presents the risk of imploding glassware. All glassware used during vacuum operations must be thoroughly inspected prior to each use. Glass that is chipped, scratched, cracked, rubbed or marred in any manner must not be used under vacuum. It must be removed from service and replaced.

5.1.4. Eye protection that satisfies ANSI Z87.1, laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Latex, vinyl, or nitrile gloves may be used. Latex and vinyl should not be used when handling methylene chloride or other organic solvents, as they provide no significant protection against these solvent.

5.1.5. Exposure to chemicals must be maintained as low as reasonably achievable, therefore all samples must be opened, transferred and prepared in a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.1.6. Laboratory procedures such as repetitive use of pipets, repetitive transferring of extracts, and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

5.2. PRIMARY MATERIALS USED

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	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid (1)	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.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Sodium Hydroxide	Corrosive	2 mg/m^3 - 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.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
EDTA buffer (disodium ethylenediamine tetraacetate	Irritant	None listed	Inhalation may cause respiratory tract irritation. Contact may cause skin or eye irritation.
Phosphoric Acid (1)	Corrosive	1 mg/m^3 TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
N-1-Naphthylethylene diamine Dihydrochloride	Irritant	None Listed	Inhalation, skin contact or eye contact may all cause irritation.
Hydrochloric Acid (1)	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.
Copper (Cupric) Sulfate	Irritant	1 mg/m^3 PEL	Skin contact may cause irritation and itching. Eye contact may cause conjunctivitis, ulceration or clouding of cornea. Inhalation may cause irritation to respiratory tract, and may cause perforation or ulceration.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

Note: *The following apparati are suggested items used in the laboratory. Alternative items may be substituted.*

6.1. Electronic analytical top-loading balance, readable to 0.0001 grams for the preparation of standards.

6.2. Nuclepore Track-Etch membrane filters, 0.2-µm, 47 mm, Whatman International Ltd., catalog number 111106. Handle with care, as membranes are delicate.

6.3. Balance, electronic top-loading, readable to 0.1 grams and a capacity up to approximately 3500 grams for preparation of samples and reagents.

6.4. Beakers, 250 mL, glass, rinsed with acetone and dried before use.

6.5. Bottle; appropriate size, amber glass, with Teflon-lined cap.

6.6. Centrifuge, IEC model Centra-4B.

6.7. Centrifuge tubes, polypropylene, 50 mL capacity with screw cap; Fisher catalog number 05-539-9, or equivalent.

6.8. Filtering apparatus for 47-mm membrane filter, receiving flask, and vacuum pump/trap. Rinse the receiving flask with acetone and dry before use.

6.9. Filter assembly, 0.45 µm, 25 mm PTFE, GD/X; Whatman catalog number 6874-2504, or equivalent, and PTFE, Millipore Millex-LCR, catalog number SLCR025 NB, or equivalent.

6.10. Flasks, volumetric, glass with stopper, appropriate sizes for preparation of standards.

6.11. Alpkem Flow Solution IV automated flow analyzer, consisting of the following:

6.11.1. Automatic sampler.

6.11.2. Proportioning pump.

6.11.3. Injection module equipped with microloop.

6.11.4. Colorimeter with 540 nm filter and flow cell.

6.11.5. Reaction cartridges (#A002670); with an open tubular cadmium reactor (OTCR) (#AOW897).

6.11.6. WinFlow software system.

6.11.7. Pillow assembly filled with nitrogen gas for segmented flow analysis (SFA).

6.12. Disposable autosampler vials or culture tubes, 12 x 75 mm for samples and standards on the Alpkem autoanalyzer.

6.13. Micropipet, 100-200 μL Wiretrol.

6.14. Nitrogen gas manifold, N-Evaporator, Organomation Analytical Associates model 112.

6.15. Pipet, various sizes from 0.5 mL to 10 mL, gravimetric (disposable).

6.16. Pipet, Pasteur type, glass, 5¾" or 9" long.

6.17. Pipet, volumetric, glass, various sizes.

6.18. pH meter.

6.19. Spatula, micro, stainless steel; for weighing of analytical standards.

6.20. Syringe, 10-cc (disposable), B-D product # 9604 or equivalent.

6.21. Test tube, glass, 16 x 100 mm (16 mL), with Teflon lined screw cap.

7. REAGENTS AND STANDARDS

7.1. When available, pre-made, commercially prepared reagents are purchased.

7.2. Acetone, pesticide quality or equivalent.

7.3. Brij-35, polyoxyethylene 23 lauryl ether, 30% solution, Fisher, reagent grade or equivalent.

7.4. Methanol, pesticide grade or better.

7.5. Water, organic-free, reagent quality or better.

7.6. Sodium hydroxide, 1N, aqueous solution. Prepare by dissolving 20.0 grams of sodium hydroxide pellets into a 500 mL volumetric flask with reagent water. Mix well. Store the solution in a plastic bottle, label, and cap tightly. The solution is stable for up to 6 months.

7.7. Sodium hydroxide, 15N, aqueous. Prepared by dissolving 150 g of sodium hydroxide pellets into a 250 mL volumetric flask with deionized water; mix well. Store the solution in a plastic bottle, and cap tightly. The solution is stable for up to 1 year.

WARNING: Sodium hydroxide solution will get extremely hot and give off irritating fumes. Dissolve sodium hydroxide pellets into at least 200 mL of water in the volumetric flask, dissolve the pellets, and dilute to volume. Prepare the solution in the hood.

7.8. Sulfuric acid, 2N, aqueous. Prepared by diluting 28 mL of concentrated sulfuric acid in a 500 mL volumetric flask with reagent water; mix well. Store the solution in a glass bottle, and cap tightly. The solution is stable for up to 6 months.

WARNING: Carefully, add sulfuric acid to water in the volumetric flask, mix well, and dilute to volume. A violent reaction can occur when adding water to concentrated acid. Prepare the solution in the hood.

7.9. Ammonium chloride-EDTA stock solution (buffer solution). Prepare by dissolving 85.0 g of ammonium chloride and 1.0 g of disodium ethylenediamine tetraacetic acid dihydrate (EDTA) in approximately 800 mL of deionized water in a 1-L volumetric flask. Adjust the pH to 8.5 by adding concentrated ammonium hydroxide solution dropwise (monitor with a pH meter) and dilute to the 1 liter mark with deionized water. Filter solution prior to use. The solution is stable for up to 1 year.

7.9.1. Ammonium chloride-EDTA working solution (working buffer solution). Working buffer is prepared by adding 1 mL Brij-35 per 500 mL stock buffer solution. Working buffer is good for 1 week.

7.10. Sulfanilamide reagent. Prepare by adding 100 mL of 85% phosphoric acid in a 1 liter flask containing at least 600 mL of deionized water, mix gently, and add 40.0 g of sulfanilamide and 2.0 g of N-1-naphylethylenediamine dihydrochloride (NED). Mix well until the reagents dissolve, and bring the volume to 1-liter mark with deionized water. This solution is light sensitive; store in an amber glass bottle. The solution is stable for two months. Discard when severe discoloration (brown) occurs prior to the two month shelf life.

7.11. Hydrochloric acid, 0.5 N solution. Prepare by diluting 4.15 mL of concentrated hydrochloric acid (HCl) into a 100 mL volumetric flask with deionized water.

WARNING: Carefully add hydrochloric acid to water in the volumetric flask containing deionized water, mix well, and dilute to volume. Prepare the solution in the hood as HCl fumes are corrosive.

7.12. Copper sulfate, 2% w/v, aqueous. Prepare by dissolving 20 g of copper sulfate ($CuSO_4 \cdot 5H_20$) in a 1000 mL volumetric flask with deionized water.

7.13. Activating the OTCR.

7.13.1. Using a 10 mL luer-lock syringe and ¼" 28 luer female fitting, slowly flush the OTCR with 10 mL of reagent water until no debris is seen exiting the OTCR.

7.13.2. Slowly flush the OTCR with 10 mL of the 0.5 N HCl solution, followed by 10 mL of reagent water. Do not allow the HCl solution to remain in the OTCR for more than a few seconds, as it can cause damage to the cadmium surface.

7.13.3. Slowly flush the OTCR with 10 mL of 2% cupric sulfate solution. Leave this solution in the OTCR for approximately 5-10 minutes.

7.13.4. Forcefully flush the OTCR with 10 mL of stock buffer solution to remove any loose copper that may have formed within the reactor. Continue to flush until all debris is removed.

7.13.5. The OTCR should be stored filled with reagent water when not in use.

7.13.6. Activation of the OTCR is not necessary for every analysis, but may be necessary if low reduction efficiency is observed (see Section 10.5.5).

WARNING: Waste containing copper sulfate may not be poured down the drain, but must be placed in a suitable waste container for proper disposal.

7.14. Preparation of Nitrate and Nitrite Standards.

7.14.1. Use a commercially available certified 1000 mg/L stock nitrate solution. Expiration date is one year from opening, or the manufacturer's expiration date if earlier.

7.14.2. Use a commercially available certified 1000 mg/L stock nitrite solution. Expiration date is one year from opening, or the manufacturer's expiration date if earlier.

7.14.3. Prepare an Intermediate Standard of nitrate plus nitrite at 10 µg/mL as N, by diluting 0.5 mL of each 1000 µg/mL stock solution to a final volume of 100 mL with deionized water. Prepare fresh monthly using volumetric glassware. If using the auto-diluter mode on the Alpkem, the instrument will prepare the 10 ppm Nitrate-Nitrite standard daily.

7.14.4. Prepare Working Standards monthly from the 10 µg/mL intermediate standards with deionized water into each volumetric flask as follows:

Standard ID	Aliquot (mL)	Final Volume (mL)	Conc. (mg/L as N)
A	20	100	2.0
B	10	100	1.0
C	4.0	100	0.4
D	2.0	100	0.2
E	0.50	100	0.050
G	0	---	Blank

7.14.5. Date and stamp all working standards to ensure integrity and timely disposal. Record standard tracking identifiers on worksheets and logbooks. If using the

auto-diluter mode on the Alpkem, the working standards will be prepared daily at the following concentrations for the 10 mg/L intermediate solution: 0.05 mg/L, 0.2 mg/L, 0.4 mg/L, 1.0 mg/L and 2.0 mg/L.

7.15. Preparation of nitrocellulose standards.

7.15.1. Nitrocellulose in neat form may be ordered through Theatre Effects, item number FP-11, as flash cotton. It is shipped 'wet' for safety. The nitrogen assay of nitrocellulose must be available or be analyzed by a reputable testing laboratory, such as Marine Science Institute at Santa Barbara. If the assayed nitrocellulose amount is less than 10%, reject the material.

7.15.2. To prepare nitrocellulose stock solution, the flash cotton must be dried, unless the moisture content is known. Dry a small portion at room temperature in a dessicator containing Drierite (or other drying agent) under vacuum for a minimum of several days. *Do not use heat to dry nitrocellulose.*

7.15.3. Prepare a stock solution of nitrocellulose at 500 µg/mL in acetone. Carefully weigh 50 mg of the dried nitrocellulose on a weighing boat, transfer to a 100-mL volumetric flask, and dissolve the nitrocellulose in acetone. **NOTE:** *It may be required to shake the solution for approximately 4 to 6 hours to dissolve the NC into solution.* Store the stock solution in an amber glass bottle at 2 to 6°C. The stock solution is stable for six months.

7.16. Reference Standards

7.16.1. Prepare a reference standard to verify the concentration and identity of the standards and spike solutions above.

7.16.2. If a secondary source is not available, a separate intermediate stock solution may be made from the same neat by another chemist or from a neat with a different vendor or lot number. A pre-prepared solution from an approved source can also be use as a second verification standard.

7.17. Prepare the reference standard as described in Section 7.14 as applicable.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Aqueous or soil samples are collected in glass containers, sealed with Teflon-lined screw caps, and stored at 2-6°C until extraction. Other liners such as aluminum foil are acceptable.

8.2. Aqueous or soil samples should be extracted and analyzed within 28 days from collection. This holdtime is recommended only, based on method 353.2. The nitrocellulose standard has demonstrated stability up to 6 months. Any deviations from

this holdtime will be noted and evaluated in conjunction with client requirements. The samples must be analyzed 48 hours after the completion of the hydrolysis step.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.2. Quality Control Batch

The batch is a set of up to 20 field 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 particular samples for MS/MSD, the batch may contain multiple MS/MSDs. See policy WS-PQA-003 for further definition of the batch.

Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the QC Program document (WS-PQA-003) for further details of the batch definition.

9.3. Control Limits

In-house historical control limits must be determined for matrix spikes and laboratory control samples (LCS). Refer to policy WS-PQA-003 for more details.

9.3.1. These limits do not apply to dilutions (except for tests without a separate extraction), but matrix spike recoveries will be reported unless the dilution is more than 5X.

9.3.2. All LCS and MS recoveries (except for dilutions) must be entered into QuantIMS or other database so that accurate historical control limits can be generated. For tests without a separate extraction, matrix spikes will be reported for all dilutions.

9.3.3. Refer to the QC Program document (WS-PQA-003) for further details of control limits.

9.4. Method Blanks

One method blank must be processed with each preparation batch. The method blank consists of reagent water for aqueous samples. The method blank is carried through the entire analytical procedure. 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 must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 10% of the measured concentration of that analyte in the associated samples, whichever is higher. Certain programs, such as USACE, may require a more stringent evaluation of the method blank, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit.

- Re-preparation and reanalysis of any samples with reportable concentrations of analytes less that 10 times the value found in the method blank is required unless other actions are agreed with the client.
- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported. This must be documented in the NCM program.
- If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all positive results in associated samples are flagged with a "B", and appropriate comments may be made in a narrative to provide further documentation.

9.4.1. Refer to the QC Program document (WS-PQA-003) for further details of the corrective actions.

9.4.2. Aqueous method blank reporting limit = 0.50 mg/L.

9.4.3. Solid method blank reporting limit = 5.0 mg/kg.

9.5. Laboratory Control Samples (LCS)

9.5.1. For each batch of samples, analyze an LCS. The LCS contains a representative subset of the analytes of interest, and must contain the same analytes as the matrix spike. If any analyte is outside established control limits, the system is out of control and corrective action must occur.

9.5.2. If any analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur:

- Check calculations.
- Check instrument performance.
- Reanalyze the LCS, and if still outside of control limits.
- Evaluate the data, and/or
- Re-prepare and reanalyze all samples in the QC batch.

9.5.3. Data may be reported with an anomaly in the event that the LCS recoveries are high and the analyte of concern is not detected in field samples.

9.5.4. The analyst should evaluate the anomalous analyte recovery for possible trends.

9.5.5. If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.

9.5.6. If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5.7. Refer to the QC Program document (WS-PQA-003) for further details of the corrective action.

9.6. Matrix Spikes

For each QC batch, analyze a matrix spike and matrix spike duplicate (MS/MSD). Spiking compounds and levels are given in the appendices. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory-specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed.
- If the recovery for any component is outside QC limits for both the MS/MSD and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.
- If an MS/MSD is not possible due to limited sample, then an LCS duplicate may be analyzed if required by the program or client.
- The MS/MSD must be analyzed at the same dilution as the unspiked sample, unless the matrix spike components would then be above the calibration range.

9.6.1. If the amount of an analyte found in the unspiked sample is greater than 4 times the amount of spiked analyte added, then routine control limits do not apply and recoveries are not evaluated. Other analytes in the MS and MSD must still be reported. File an NCM stating that the 4X rule was applied. This NCM must be included in the final report.

9.7. Insufficient Sample

If insufficient sample is available to process a MS/MSD, then a second LCS may be processed, if precision data is required by the client. The LCS pair is then evaluated according to the MS/MSD RPD criteria. Use of an LCS pair in place of an MS/MSD must be documented using Clouseau.

9.8. Initial Calibration Verification (ICV) -- When available, a second source standard at or near the mid-point of the calibration is analyzed with the initial calibration curve. Each component of the second source calibration must be within ± 10% of its expected value. Corrective actions for the ICV include:

- Rerun the ICV.
- Remake or acquire a new ICV.
- Evaluate the instrument conditions.
- Evaluate the Initial Calibration Standards.

9.9. Nonconformance and Corrective Action

Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the QA and Department Manager.

9.10. Quality Assurance Summaries

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

9.11. QC Program

- Further details of QC and corrective action guidelines are presented in the QC Program document (WS-PQA-003). Refer to this document if in doubt regarding corrective actions

10. CALIBRATION

10.1. The instrument optimization is part of the instrument set-up and pre-programmed internally.

10.2. Instrument calibration is done daily before any samples are analyzed. The calibration curve consists of five (5) standards and a blank. The correlation coefficient of the curve must be at least 0.995 or greater.

10.3. The Initial Calibration Verification Standard (ICV) and Initial Calibration Blank (ICB) must be analyzed immediately following the initial calibration and prior to sample analysis.

10.3.1. The ICV/CCV standard concentration is at or near the mid-point concentration of the calibration curve and must be within 10% of the expected value. If not,

correct the problem and re-analyze any affected samples back to the last valid CCV. Perform a new multi-point calibration if the ICV fails upon re-analysis.

10.3.2. The reagent blank includes all the reagents added after extraction and is used as the ICB and CCB. The ICB/CCB values must be less than the reporting limit.

10.4. A Continuing Calibration Verification (CCV) and the CCB are analyzed following every ten or fewer samples and at the end of the run. This standard must be within 10% of the expected value.

10.5. Corrective actions and suggestions for repeated failures of calibration verifications and calibration blanks.

10.5.1. Check for contamination in the reagents and standards.

10.5.2. Be sure all reagents were prepared correctly and have not expired.

10.5.3. Check the system for obvious problems, such as plugs, leaks, and worn or degraded pump tubes.

10.5.4. Identify samples that may have deactivated the reduction column. Samples may need to be diluted and/or re-extracted. Consult with the Department Manager before continuing.

10.5.5. Analyze a 2 µg/mL nitrite standard and compare to a 2 µg/mL nitrate standard. If the results differ by more than 15%, the column has deteriorated and needs to be reactivated with copper sulfate.

10.5.6. If you are unable to locate and solve the problem, consult with your Department Manager for further corrective actions.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of a 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 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. This SOP was written for the Alpkem Flow Solution IV system and must be followed in order to work with the existing instrument software. Any deviations may require modifications to the instrument program. Also, any changes in the program may require alterations in this SOP. Comparable instrumentation may be used if data quality objectives and method performance criteria can be met.

11.4. Aqueous Sample Preparation

11.4.1. Obtain samples from sample receiving. Allow the samples to equilibrate to room temperature.

11.4.2. Prepare a method blank (MB) for the batch by measuring 100 mL of reagent water into a mixing cylinder.

11.4.3. Prepare the LCS (and LCSD, if needed), by spiking a clean mixing cylinder with 400 µL of the 500 µg/mL nitrocellulose stock solution to yield 2.0 ppm NC (or 0.20 µg/mL N), assuming the assayed NC amount is 10%. Air dry cylinder, then add 100 mL of reagent water. Mix the contents well by shaking vigorously and/or sonicate in a water bath for approximately 5 minutes.

***NOTE**: Assayed nitrocellulose may vary, therefore the preparation concentration will vary.*

11.4.4. Prepare cylinders for the MS and MSD by spiking two clean cylinders with 400 µL of the 500 µg/mL nitrocellulose stock solution. Allow the cylinders to air dry prior to adding sample aliquots (as in Section 11.4.5, below).

11.4.5. For each field sample, shake the sample well and quickly measure 100 mL into a 100-mL mixing cylinder or graduated cylinder.

11.4.6. Mix the contents of the MS and MSD cylinders well by shaking vigorously and/or sonicating in a water bath for approximately 5 minutes.

11.4.7. Add 50 µL of Brij-35 solution to each sample, MB, LCS/LCSD, and MS/MSD. Mix the contents well.

11.4.8. Set up the filtering apparatus with a Nuclepore membrane filter.

Note: The Nuclepore membrane filter is very delicate. Handle with care when setting up the apparatus. Do not allow the membrane filter to go dry during the filtration.

11.4.8.1. Mix the water sample well and pour it into the filter assembly.

11.4.8.2. Turn the vacuum on low, and allow the sample to filter through the assembly.

11.4.8.3. Rinse the sample container with 15 mL of reagent water. Filter. Repeat two more times.

11.4.8.4. Wash the filter with 100 mL of reagent water, and stop the flow just before drying.

11.4.9. Carefully remove the filter with tweezers and transfer it to a 250 mL glass beaker. ***The Nuclepore membrane filter is very delicate. Handle with care.*** Rinse the inner surface of the filter holder with approximately 20 mL of acetone and add to the beaker.

11.4.10. Cover the beaker with a watch glass. Let the filter stand submerged in acetone for 1 hour, swirl the solution occasionally.

11.4.11. Transfer the acetone extract to a 50 mL centrifuge tube, rinse the filter and beaker with two 15 mL portions of acetone, and transfer each portion to the centrifuge tube. Do not exceed the 50 mL capacity of the tube.

11.4.12. Store the extracts in the refrigerator at 2-6°C until ready for N-Evap and hydrolysis.

11.5. Soil/Solid Sample Preparation

11.5.1. Allow the soil sample to equilibrate to room temperature.

11.5.2. Prepare 50 mL centrifuge tubes for the spiked samples – LCS (/LCSD) and MS/MSD. Add 1.0 mL of the 500 µg/mL solution into an empty tube. Allow the solution to dry under a gentle stream of nitrogen.

11.5.3. Weigh 10 g of soil sample into a 50 mL centrifuge tube.

11.5.3.1. For the MB and LCS/DCS, use crushed, ground Ottawa sand as the control matrix.

11.5.4. Wash the samples and QC aliquots with two 20 mL aliquots of 1:1 methanol-water solution. Shake the tube vigorously for approximately 10 seconds and on the platform shaker for 10 minutes at approximately 240 rpm. Centrifuge at approximately 3500 rpm for 20 minutes, decant carefully and discard the washing solution.

Note: If the solids (particularly solids as wipes) are too loose following centrifuging, it may be necessary to add crushed, ground Ottawa sand to aid the packing of the

solids, which improves the recovery of nitrocellulose. A 10 g aliquot of sand should be sufficient.

11.5.5. Extract the washed residue by adding 15 mL of acetone, shake the tube vigorously for 10 seconds, and allow the contents to stand for 1 hour before proceeding.

11.5.6. Shake the samples on the platform shaker for 10 minutes at approximately 240 rpm, centrifuge at approximately 3500 rpm for 10 minutes, and decant the acetone into a 50-mL centrifuge tube.

11.5.7. Extract the soil two more times with 15 mL portions of acetone, shake vigorously for 10 seconds and on the platform shaker for 10 minutes at approximately 240 rpm. Centrifuge at approximately 3500 rpm for 10 minutes, and pool the acetone in the 50 mL centrifuge tube.

11.5.8. Store the extracts in the refrigerator at 2-6°C until ready for N-Evap and hydrolysis.

11.6. N-Evap and Hydrolysis of Nitrocellulose to nitrate-nitrite

Note: The holding time for the extraction and analysis of samples is 28 days from sampling. Once the extracts are hydrolyzed, they must be analyzed within 48 hours. Coordinate with the General Chemistry Department Manager to ensure that samples can be analyzed within the required holding time.

11.6.1. Set the N-Evap water bath at 50 - 55ºC.

11.6.2. Add 2.0 mL of 1N NaOH to the acetone extracts in the 50 mL centrifuge tubes, and mix the contents well. *Do not start this step unless the samples can be analyzed within 48 hours after the completion of the hydrolysis step.*

11.6.3. Evaporate the acetone extracts under a gentle stream of nitrogen on the N-Evap in a water bath at 50 ± 5ºC. When the volume is reduced to 1 or 2 mL, turn off the nitrogen, and continue heating the extracts for an additional 1 hour.

Note: The chemical reaction step is now completed. Document the time of completion on the benchsheet. Analyze within 48 hours.

11.6.4. Bring each sample up to approximately 10 mL with reagent water. Mix the solution well, and adjust the pH to between 6 and 8 with 2N sulfuric acid and/or 1N sodium hydroxide. Monitor the pH adjustment using a meter.

11.6.5. Adjust the final volume to 40 mL with reagent water, and mix well. The preparation factor (V_f/W_x) is 40 mL/100 mL for aqueous samples, and 40 mL/10 g for solid samples. (V_f = final extract volume, W_x = initial sample

weight or volume)

11.6.6. Filter an aliquot of solid extract through a Whatman GD/X syringe filter on a Millipore Millex-LCR filter assembly into a 16-cc test tube, and submit the filtered extracts for analysis. Filter an aliquot of aqueous extract through a Millipore Millex-LCR filter assembly.

11.6.6.1. The excess solution in the centrifuge tubes may be saved until the analysis of nitrate plus nitrite is complete. Many times, solid extracts are very difficult to filter through Millipore Millex-LCR filter without the Whatman GD/X.

11.7. The extracts are stored at 2-6°C until ready for analysis of nitrate/nitrite. Notify the Department Manager and/or the analyst the NC samples are ready for analysis. Submit the extraction paperwork to the analyst.

11.8. Instrument Start-Up

11.8.1. The instrument is to be set up and operated in accordance with the manufacturer's instructions. Install the nitrite and nitrate/nitrite cartridges according to manufacturer's instructions, following the SFA methodology. The reduction coil must be used to measure the nitrate/nitrite.

11.8.2. Inspect the cartridges for proper connections. Make sure that there is sufficient volume for all reagents for the entire run. All reagents and standards must be within the expiration dates.

11.8.3. Prepare the working standards as stated in Section 7.13.4.

11.8.4. Turn on the power to the system unit, pump, autosampler, and the software system. The heating coil is not needed and must be turned off.

11.8.5. Connect the buffer lines to the startup solution reagent bottle containing 1000 mL reagent water and 2 mL Brij-35. Connect the color reagent lines to the reagent bottle containing reagent water.

11.8.6. Fasten down the pump tube cassettes. Make sure the reagent tubes are in good working condition.

11.8.7. Load the nitrate plus nitrite method in the computer. You should see the NO_2+NO_3 and NO_2 backgrounds on the computer screen. Pump reagent water through the system until a stable baseline is obtained.

11.8.8. Connect the nitrate/nitrite buffer line to the ammonia chloride buffer. Pump the reagents through all lines until a stable baseline is obtained.

11.8.9. Turn off the pump and connect the OTCR to the Nitrate-Nitrite cartridge. The instrument is ready for analysis when a stable baseline is obtained with the OTCR and all reagents.

11.9. Analysis

11.9.1. Load the autosampler with the working standards, or empty cups and stock standards if using the auto-dilution mode.

11.9.2. Load the autosampler with samples and QC aliquots according to the sample table created in WinFlow. Enter dilution factors if applicable.

11.9.3. Start the analysis. The instrument will analyze the standards and continue with sample analysis if the correlation coefficient is > 0.995. If the calibration curve is not acceptable, correct the problem and recalibrate. The instrument should be monitored periodically to make sure that the ICV/CCVs are in control and that no other problems arise. The calibration statistics and raw data should be printed at the end of the run.

11.9.4. Check the printout for off-scale samples. Dilute, and rerun if necessary.

11.9.5. If additional samples or dilutions are to be analyzed, reload the autosampler and enter the new tray information. Since the instrument is already calibrated, you may analyze another batch of samples.

11.10. Shut Down

11.10.1. Turn the pump off and remove the OTCR.

11.10.2. Place all reagent lines in the deionized water and pump at normal speed for at least 5 minutes.

11.10.3. Drain the water out of the wash vessel.

11.10.4. Turn off the units and unfasten the pump tube cassettes from the pump. Release the tension levers.

11.10.5. Clean up the work area and replace any reagents, which have been depleted.

WASTE GENERATED MUST BE COLLECTED IN SPECIAL WASTE STREAM CONTAINERS AND STORED PROPERLY.

12. CALCULATIONS/DATA REDUCTION

12.1. For nitrocellulose (NC) conversion, use only the nitrate/nitrite (NO_3+NO_2) concentration.

12.2. The amount of NC found in the sample is derived from the amount of N (nitrate/nitrite) measured, using the following formula

Formula 1 **NC** = (N / Fp) x (Vf / Wx)

Where: NC = nitrocellulose concentration in µg/mL or µg/g (ppm).
N = nitrate plus nitrite concentration in µg/ml.
Vf = final extract volume (mL).
Wx = Sample mass (grams for soil) or volume (mL for aqueous).
Fp = Percent nitrogen factor in nitrocellulose (assay, such as 0.10 for 10% N).
Fp may vary depending on the lot.

12.3. If the prep factor Pf is already taken into consideration during the analysis, where:

Formula 2 Pf = Vf / Wx

then:

Formula 3 NC = N / Fp

12.4. For % recovery and % RPD calculations, see policy WS-PQA-003.

12.5. The reporting limit for nitrocellulose is dependent on the reporting limit of nitrate/nitrite. The reporting limit for nitrate/nitrite is 0.05 mg/L (ppm). With the final aqueous extract concentration/dilution factor at 100 mL/40 mL, the reporting limit is calculated by using formula 1, assuming the assay of NC is 10% N, and inserting a RL buffer factor of 2.5.

NC = (N / Fp) x (Vf / Wx) x 2.5

NC = ((0.05 mg/L)/0.100) x (40 mL/100 mL) x 2.5 = 0.50 µg/mL NC

12.6. With the final soil extract concentration/dilution factor at 10g/40 mL, the reporting limit is calculated using formula 1, assuming the assay of NC is 10% N;

NC = ((0.05 mg/L)/0.100) x (40 mL/10 g) x 2.5 = 5.0 µg/g NC

13. METHOD PERFORMANCE

13.1. 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 expertise.

13.2. The laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix

B, and further defined in SAC-QA-0006 and SOP CA-Q-3-006. MDLs are available in the Quality Assurance department.

14. POLLUTION PREVENTION

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.

15. WASTE MANAGEMENT

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

15.1. Water, hydrochloric acid solution, cupric sulfate solution and EDTA stock buffer solution used to rinse the OTCR. This is collected in a one liter bottle until full or for no more than one year, then transferred to the blue plastic metals acidic waste drum. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.2. Miscellaneous disposable glassware, Anodisc membrane filters, disposable centrifuge tubes, filter discs, chemical resistant gloves, bench paper and similar materials that may or may not be contaminated/hazardous. Place contaminated materials into a contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the lab trash into the steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.3. Extracted soil samples in centrifuge tubes, contaminated with methanol and acetone. These are transferred to the waste disposal area for lab pack and shipment.

15.4. 1:1 water:methanol solution used to wash soil samples prior to extraction. Decant the washing solution into the HPLC waste carboy. When full, or after no more than one year, dump into the blue plastic HPLC collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.5. Acidic waste from the auto-analyzer. This is collected in a 1-gallon plastic coated carboy. When the carboy is full, or after no more than one year, move the carboy to the waste collection area, where it will be lab-packed into a drum for shipment.

15.6. Unused sample extract in centrifuge tubes, which is retained until after analysis is completed. These are transferred to the waste collection area, where they will be lab-packed into a drum for shipment.

16. REFERENCES/CROSS REFERENCES

16.1. "Quality Control Program", Policy WS-PQA-003.

16.2. "Determination of Nitrocellulose in Soil by Autoanalyzer", Leo O'Shea, Raytheon Laboratories, Boothwyn, PA, August 1997.

16.3. "The Determination of Nitrocellulose in Water by Colorimetric Autoanalyzer", DataChem Laboratories, Version 1.0, January 15, 1991.

16.4. "The Determination of Nitrocellulose in Soil by Colorimetric Autoanalyzer", DataChem Laboratories, Version 1.0, January 8, 1991.

16.5. EPA MCAWW 353.2 Nitrogen, Nitrate-Nitrite (Colorimetric, Automated, Cadmium reduction).

16.6. Standard Method 4500-NO_3 F. Automated Cadmium Reduction Method, 18th Edition 1992.

16.7. Method source: OI Analytical Document #319437 equivalent to EPA method 353.2.

17. METHOD MODIFICATIONS

17.1. Deviations from reference methods.

17.1.1. The hold time for samples to be analyzed by this method is 28 days, and 48 hours after the hydrolysis step. The O'Shea method suggests the hold time is 40 days and should be analyzed within 24 hours after the chemical reaction (hydrolysis step), whereas, the method suggests that the samples be analyzed within 28 days. The holding time selected by this laboratory is defined by the EPA for nitrate/nitrite, method 353.2.

17.1.2. An Alpkem Flow Solution IV is used in place of a Technicon Autoanalyzer II. Both instruments are compatible and designed for nitrate plus nitrite analysis.

17.1.3. Linear range is designed based on the manufacturer's recommendation of 0.05 to 2.0 mg/L instead of 0.05 to 10 mg/L.

17.1.4. Absorbance is at 540 nm instead of 550 nm.

17.1.5. Sodium hydroxide is used in place of ammonium hydroxide for pH adjustment. There is no impact on the chemical reaction.

17.1.6. Sulfuric acid is used in place of hydrochloric acid for pH adjustment. There is no impact on the chemical reaction.

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17.1.7. Reagent preparations are performed according to the manufacturer's instructions and may differ from the method.

17.1.8. Shelf life for calibration standards is changed to monthly based on the in-house stability study performed for these analytes.

17.1.9. Preservation with chloroform is omitted. Stock standards are stable for at least 6 months without preserving with chloroform.

17.1.10. This SOP is dedicated for the preparation and analysis of nitrocellulose as nitrate/nitrite. The methods do not clearly define the standard preparation, calibration, and acceptance criteria. The analytical protocols for Nitrate plus Nitrite, method (353.2) are adopted for nitrocellulose.

17.2. Deviations from reference method; O'Shea method.

17.2.1. The nitrocellulose stock solution is valid for up to six months rather than 1 week.

17.2.2. Nanopure water is used instead of deionized water or ASTM Type I water.

17.2.3. When the soil sample is washed and extracted, it is vortexed for 10 seconds and shaken on the platform shaker for 10 minutes, rather than vortexed 15 seconds without any further shaking.

17.2.4. The final extract volume for water and for soil is 40.0 mL instead of 100 mL to achieve a lower reporting limit; 0.50 mg/L NC for aqueous, and 5.0 mg/kg NC for soil.

17.3. Deviations from reference method

17.3.1. To fortify the aqueous samples, the spiking solution is added to a clean mixing cylinder and allowed to dry before adding the 100 mL water sample or the controlled water sample prior to extraction.

17.3.2. Soak the residues on the Anodisc membrane filter in acetone for 1 hour instead of 10 minutes.

17.3.3. A 10 gram soil sample is washed and extracted instead of a 0.5 gram, and washed with methanol instead of water.

17.3.4. After vortexing for 10 seconds, the sample is also shaken on the platform shaker for 10 minutes.

17.3.5. The soil sample is soaked in acetone for an hour or longer rather than 90 minutes.

17.3.6. 2 mL rather than 1 mL of the 1N sodium hydroxide is added to the acetone extracts, and after the acetone dissipates the basic extracts are heated for an additional 1 hour to complete the chemical reaction (hydrolysis of nitrocellulose to nitrate plus nitrite)

17.3.7. The final volume for water is adjusted to 40.0 mL with nanopure water after the pH adjustment to between 6 and 8, instead of transferring to 100-mL volumetric flask, adjusting the volume to mark with ASTM Type I water, and adjusting the pH to between 7 and 9.

18. ATTACHMENTS

18.1. Table 1- Aqueous and Soil LCS and MS/MSD Spike Levels

18.2. Flow Chart 1- Preparation of Samples

18.3. Flow Chart 2- Nitrate Plus Nitrite by Alpkem Flow Solution IV Autoanalyzer

19. REVISION HISTORY

19.1. WS-WC-0050, Revision 3.1, Effective 05/01/2009

19.1.1. Section 7.1 - inserted "When available, pre-made, commercially prepared reagents are purchased."

19.1.2. Section 7.13.4 - Deleted 0.025 mg/L standard from table.

19.1.3. Section 12.5 and Section 17.2.4 - inserted buffer factor of 2.5 which changed RL from 0.2 and 2.0 to 0.5 and 5.0 for aqueous and soil samples respectively.

19.2. WS-WC-0050, Revision 3, Effective 2/29/2008

19.2.1. This SOP format has been updated to the new TestAmerica format.

19.3. SAC-WC-0050, Revision 2.2, Effective 4/13/07

19.3.1. Updated to reflect current reporting limit (Section 9.4.3)

19.3.2. Updated to reflect current practice. Connect the nitrate/nitrite buffer line to ammonia chloride buffer. Pump the reagents through all lines until a stable baseline is obtained.

19.4. SAC-WC-0050, Revision 2.1, Effective 1/11/05

19.4.1. Updated equiptment list(Section 6.2, 11.4.8, 11.4.9, 15.2, 17.3.2)

19.5. SAC-WC-0050, Revision 2, Effective 8/12/03

19.5.1. Fixed grammatical errors, improved flow of SOP, updated page formatting.

19.5.2. Updated safety, pollution, and waste disposal sections in accordance with recent EH&S requirements.

19.6. SAC-WC-0050, Revision 1, Revised 6/28/01

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TABLE 1

AQUEOUS - LCS AND MS/MSD

Test Components	NC Spike Level, mg/L
Nitrocellulose	2.0

SOIL - LCS AND MS/MSD

Test Components	NC Spike Level, mg/Kg
Nitrocellulose	50

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Flow Chart 1
Flow Diagram- Preparation of Samples

AQUEOUS SAMPLES

FORTIFY cylinders for spiked samples, allow cylinders to DRY prior to sample addition.

MIX the aqueous samples well and measure 100 mL into mixing cylinders

Add Brij-35 solution, mix well and FILTER through Anodisc membrane. WASH with water

DISCARD water

SOAK membrane filter in ~20 mL acetone for 1 hour.

EXTRACT filter 2 more times with acetone

Discard Filter

SOLID SAMPLES

WEIGH 10 g solid into 50-mL tubes

FORTIFY spike samples, allow to DRY.

WASH with MeOH 2x, VORTEX 10 sec, SHAKE 10 min, CENTRIFUGE 20 min, DECANT MeOH

DISCARD MeOH wash solution

EXTRACT with Acetone, VORTEX 10 sec, let STAND for at least one hour.

SHAKE 10 min, CENTRIFUGE 10 min.

EXTRACT solid residue 2 more times with acetone, VORTEX 10 sec, SHAKE 10 min, CENTRIFUGE 10 min.

DISCARD soil residue

COMBINED

DECANT Acetone into 50-mL tubes

Acetone Extracts in 50-mL tubes ready for N-evap and Hydrolysis

Add 2 mL 1N NaOH, mix well

N-Evap at 50C until acetone dissipated, (1-2 mL), heat 1 additional hour

RECORD time when hydrolysis is completed. 48 hour analytical hold time starts here.

Dilute to 10 mL with water, mix well, adjust pH to 6-8 (pH meter)

ADJUST volume to 40 mL with water, MIX well.

FILTER a portion into 16-mL tubes.

SUBMIT to GenChem for nitrate/ nitrite analysis.

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Flow Chart 2
Nitrate Plus Nitrite By Alpkem Flow Solution IV Autoanalyzer