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New England District
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QUALITY ASSURANCE PROJECT PLAN

Volume IIA
Appendix A, Continued

29 March 2001 (DCN: GE-021601-AAHM)

Revised May 2003 (DCN: GE-022803-ABLZ)

Environmental Remediation Contract
General Electric (GE)/Housatonic River Project
Pittsfield, Massachusetts

Contract No. DACW33-00-D-0006

WESTON SOLUTIONS℠

QUALITY ASSURANCE PROJECT PLAN, FINAL (REVISED 2003)

Volume IIA—Appendix A, Continued

October 27, 1999 (DCN: GEP2060499-AAIY)

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Contract No. DACW33-00-D-0006

Prepared for

U.S. ARMY CORPS OF ENGINEERS
New England District
696 Virginia Road
Concord, MA 01742-2751

Prepared by

WESTON SOLUTIONS, INC.
One Wall Street
Manchester, NH 03101-1501

W.O. No. 20125.257.103.1625

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APPENDIX A-82

STANDARD OPERATING PROCEDURE FOR INTERSTITIAL WATER EXTRACTION

of total organic carbon. After each cycle, the sediment was remixed with DDI water, shaken for 24 hr, and then processed as previously described. Three replicates were taken through four leach cycles in anaerobic sediment testing. For aerobic sediment, five replicates were taken through a single leach cycle.

Interstitial water extraction

16. Interstitial water samples for metal and organic contaminant analysis were obtained by centrifugation of the New Bedford sediment. To obtain samples for metals from anaerobic New Bedford sediment, triplicate 250-ml polycarbonate centrifuge tubes fitted with a leakproof, airtight top were loaded with sediment in a glove box under a nitrogen atmosphere. The tubes were then centrifuged at 13,000 × g for 30 min, and the supernatant was filtered under a nitrogen atmosphere through a 0.45-μm pore size membrane filter. The filtrate was then acidified to pH 1 with concentrated Ultrex grade nitric acid and stored in plastic bottles until analyzed. Procedures for obtaining interstitial water for metals analysis from aerobic New Bedford sediment were similar to those described for anaerobic sediment, except that all steps in the aerobic operation were conducted without the use of nitrogen.

17. Interstitial water for analysis of organic contaminants was obtained by centrifugation of anaerobic New Bedford sediment in 450-ml stainless steel centrifuge tubes. Six tubes were loaded with sediment, centrifuged for 30 min at 6,500 × g, then filtered through a Whatman GF/D glass-fiber prefilter and a Gelman AE glass-fiber filter with a nominal pore size of 1.0 μm. All steps in the operation were conducted under a nitrogen atmosphere. Following filtration, the interstitial water was acidified with 1 ml of concentrated hydrochloric acid, then stored in the dark in acetone-rinsed 2-ℓ glass bottles until analyzed. Aerobic interstitial water was obtained in a similar manner, except that anaerobic conditions were not maintained during the operation.

Permeameter Testing

Loading and operation

18. Column leaching tests were conducted in divided-flow permeameters designed to minimize wall effects and provide for pressurized operation (Figure 1). The inner permeameter ring divides flow, separating the leachate flowing through the center of the column from leachate flowing down the walls,

APPENDIX A-83—STANDARD OPERATING PROCEDURE FOR FREEZE DRYING

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Freeze Drying

1. Method Reference

1.1. Methods – Based on procedure developed Lyophilization Services of New England, Inc.

2. Scope and Application

2.1. This method is recommended for high moisture content samples from lipids, polymers, proteins, natural resins, cellular components and dispersed high molecular weight compounds.

2.2. The intent of the method is to decrease the water content of a sample there by increasing the amount of dry material available for analysis.

3. Summary of Method

3.1. Samples collected in appropriate containers. Tissue samples and vegetation may require maceration before the process begins. Samples are place in 8-ounce jars frozen and placed in the freeze-drying unit. The samples remain in the unit under vacuum unit until the desired dryness is achieved.

4. Equipment and Reagents

4.1 8 oz. glass-jars with Teflon-lined lids.

4.2 Freeze drier model –Hull 8FS12C.

5. Procedure

5.1 The 8 oz. jar is filled to no more than half way with the sediment, tissue or vegetation. The lid is placed on the jar loosely to allow for air and water vapor to escape.

5.2 Samples are placed onto the pre-cool shelf at - 45°C for four hours.

5.3 The shelf is brought to a temperature of 18 ± 5°C for a time of approximately 14 hours or until sufficient moisture has been removed from the sample. The freeze drying apparatus is brought to a pressure of 150 milli-torr ±50 milli-torr for the duration of the process.

5.4 Once the samples are at an acceptable dryness, they are removed from the unit and stored at 4°C unit sample preparation (extraction or digestion) is performed. The lids are tightened prior to storage.

5.5 Alternatively, the samples can be frozen at - 10°C to preserve the hold time of the samples.

	Approval Signatures	
Laboratory Director	Peter J. Kane	Date: 4/4/00
Quality Assurance Manager	Elaine Haymes	Date: 4/4/00
Vendor		Date: 3/22/00

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APPENDIX A-84—STANDARD OPERATING PROCEDURE FOR EXTRACTION OF SOIL, TISSUES, VEGETATION, AND SEDIMENT SAMPLES BY PRESSURIZED FLUID EXTRACTION

METHOD 3545

Extraction of Soil, Tissues, Vegetation and Sediments Samples by Pressurized Fluid Extraction

1. Method Reference

1.1 Method 3545C and Method 8000B, Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Final Update III, December 1996 (USEPA, Office of Solid Waste and Emergency Response, Washington, DC).

2. Scope and Application

2.1 This method is applicable for the extraction of soil, sediment, vegetation or tissue samples for the analysis of organic compounds for a variety of analyses.

3. Summary of Method

3.1 A measured weight of sample is placed in an extraction vessel. The sample is flushed with hot pressurized solvent. The resulting extract is dried and concentrated to an appropriate extract volume for further cleanup or analysis.

	Approval Signatures	
Laboratory Director	Peter J. Kane	Date: 2/4/00
Section Supervisor	Nancy A. Rose	Date: 2/4/2000
Quality Assurance Manager	Hughes	Date: 2/4/2000

4. Sample Handling and Preservation

4.1. Samples are collected in pre-cleaned 8-ounce jars with a Teflon lined screw cap. Approximately 15-20g of sample is aliquoted for the extraction. Greater mass can be extracted using multiple cells containing equivalent portions of the sample.

5. Equipment and Reagents

5.1 Dionex ASE 200 Accelerated Solvent Extractor

5.2 Sample concentrator - apparatus for reducing sample extract volumes (KD Bath, S-Evap, N-Evap or Turbo-Vap Analytical Evaporator).

5.3 Diatomaceous earth, pelletized; Ottawa sand cleaned with methylene chloride.

5.4 Glassware - glass powder funnels; Kuderna-Danish (KD) evaporator; 10mL concentrator tube; 1mL capacity syringe; Turbo-Vap tubes; Snyder columns and 60mL "VOA-like" collection vials.

5.5 Glass wool; boiling chips; dried sodium sulfate; 2-mL capacity glass vials; screw caps and water bath (heated to ~85°C).

5.6 Methylene chloride, Acetone and Hexane – Ultra-resi grade. (DI water for rinsing.)

5.7 Tissumizer – Ultra-Turrax T-25; stainless steel cups (50mL). Black & Decker model HC3000 chopper/mincer modified with a titanium blade.

5.8 Analytical Balance- capable of weighing to 0.01g.

6. Sample Preparation: Soil/Sediment/Tissue Samples/Vegetation (Method 3545)

6.1 Tissue samples must be homogenized into a slurry or paste-like consistency before the extraction process can be performed.

6.1.1 **Bivalve** samples in most cases are frozen. If required by the project, the lengths of each shell for a sample site may be measured before the sample processing begins.

6.1.2 The shells can be shucked from the bivalve best, if is it just partially thawed. Rinse the exterior shell of the bivalve with DI water if there is any extraneous material on it. A stainless steel knife or titanium knife is used to open the bivalve. The entire contents of the bivalve are removed. Multiple specimens from each site are pooled together (unless otherwise specified for the project) into a beaker.

6.1.3 If whole **fish** or edible fillets are to be analyzed, care must also be taken to avoid any contact with material that has not been properly cleaned. Whole fish may need to be sectioned into sizes that will fit into the extraction apparatus. After the sections have been reduced to slurry, they are recombined, thoroughly mixed, and the whole fish is now ready for extraction. If fillets are received, they may require sectioning like the whole fish, if they are large. If whole fish are to be filleted, the same care must be taken to avoid any contact with non-cleaned material. The fillet knife, and the surface used for performing the fillet, must be thoroughly cleaned after each fish is processed to avoid cross-contamination between fish samples.

6.1.4 **Blubber** samples must be partially thawed before being cut into sizes that are appropriate for macerating. The same care with regard to contamination in the fish sample must be taken with the blubber samples.

6.1.5 **Target organs** such as the **liver** may require a qualified marine biologist to perform the dissection and identification of the organs of interest. Once removed from the specimen, the organs should be appropriately combined and go through the same maceration process as other materials.

6.1.6 The goal for any tissue is to have 50 to 100 grams of macerated material for the extraction process.

6.1.7 The tissuemizer must be thoroughly rinsed with methylene chloride before use. This will require a stainless steel cup filled half way with methylene chloride to be run on the unit. The mechanical mixing of the solvent will clean the unit. All the spatulas and beakers will also be solvent rinsed.

6.1.8 The actual sample grinding is done with approximately one third of the cup filled with tissue. Run the unit until the tissue is a paste or slurry. Pour the material into a screw-capped jar. Successive sample aliquots may be required to obtain sufficient material.

6.1.9 After the tissue sample homogenizing is complete, the unit must be cleaned again with methylene chloride and inspected for residual tissue or scales clinging to the unit. The unit may require disassembly, rinsing and re-assembly. Then the next sample can be processed.

6.1.10 Alternatively the Black & Decker model HC3000 chopper/mincer can be used. This has been modified with titanium blades to minimize the metals contamination for combined samples. The unit is rinsed with detergent and water followed by DI water before use and in between samples. The tissue samples are added to the unit, macerated for one minute or until a homogeneous mix is observed. It can then be transferred to a screw-capped bottle.

6.1.11 Once the tissue is homogenized, it is then processed the by the same protocol as the soil or sediment samples on the ASE extractor.

6.2 Plant materials will have to be reduced in size to fit into the extraction cell. This can be accomplished by cutting the vegetation with a knife on a Teflon board or using solvent cleaned scissors. Enough material must be produced to obtain the project specific reporting limits. Alternatively the plant material may require mechanical maceration using the chopper or the tissumizer. Examination of the tissue by the project manager in conjunction with the client will determine if this process is required.

6.3 Weigh approximately 20 grams of low moisture sample (soil or vegetation) or 15 grams of high moisture sample (sediment or tissue) into a beaker (10 grams for an Extractable Petroleum Hydrocarbon EPH) and record the actual weight used in the extraction logbook. Remember to decant any water from the top of sediment samples (unless instructed *not* to decant standing water by project specific guidelines) and discard any foreign objects such as rocks and sticks or leaves from all samples prior to determining the percent solids. Add sufficient diatomaceous earth and mix well until dry. Grind if necessary to obtain a free flowing powder. For Method Blanks and Laboratory Control Samples (LCS), aliquot approximately 20g of infusorial/diatomaceous earth and Ottawa sand or equivalent (use a representative sample weight for determining concentrations in blanks).

6.4 Use a prepared stainless steel extraction cell, cleaned by washing with soap and water between each use, rinsing with acetone to remove water, and rinsing with extraction solvent (methylene chloride) immediately prior to use.

6.5 Close the bottom end of the cell, insert the cellulose filter, and use a rod to press the filter into place at the bottom of the cell. Make sure the filter is properly seated.

6.6 Transfer the entire contents of the sample beaker to a 33mL cleaned stainless steel extraction cell fitted with the cellulose filter. Record the sample IDs and the associated cell numbers in the ASE extraction logbook. Do not attach labels to the outside of the cell. Labels may cause misalignment in the system or the label may be damaged since the entire cell is placed in an oven during the extraction.

6.7 Insert another cellulose filter using a rod to lightly press it into place on the top of each sample. Spike each cell with 1mL (or the project-specified spiking volume) of the Surrogate mix and any appropriate Matrix/LCS Spike solution.

6.8 Close the top of the cell. Caps should be hand-tightened only. Clean the rod between each sample.

6.9 Verify that the white O-rings are in place and are in good condition on the ends of the cell.

6.10 Place the extraction cells into the autosampler tray on the ASE unit. Record the autosampler position for each sample in the ASE logbook.

6.11 Load the collection tray with the appropriate number (up to 24) of 60-mL pre-cleaned, capped "VOA-like" vials with septa, labeled with the corresponding sample IDs. Labels should only be placed from 1 3/8" to 3 1/8" from the top of the closed cap of the vial, to prevent blocking of the sensors on the system.

6.12 Select the correct method on the system keypad and press start.

6.13 ASE 200 Operating Conditions:

System Pressure:	14 MPa (2000 psi)
Oven Temperature:	100°C
Oven Heat-Up Time:	5 min.
Static Time:	5 min.
Solvent:	Methylene chloride/Acetone (70:30)
Flush Volume:	60% of extraction cell volume
Nitrogen Purge:	1 MPa (150 psi) for 60 seconds
Rinse Cycle	8 mL

6.14 The sample may now be concentrated and/or solvent exchanged, then brought to the desired final volume for cleanup or analysis. The concentration can be performed using a K-D on the hot-water bath or the Turbo-Vap apparatus.

6.15 _K-D Concentration_: Place the KD flask on the KD bath with boiling chips and the Snyder column on top. The bath temperature should be 80-90°C. Macro-concentrate the sample to less than 10mL. This will take approximately 15-20 minutes. As an alternative the S-EVAP may be used to concentrate. Transfer the sample in the 10mL concentrator tube to the N-Evap unit and bring the extract to the final volume required before cleanup (refer to Table 1). *If the sample appears extremely viscous and reduces in volume very slowly then a final volume of 5 or 10mL should be used to salvage any surrogate data. See your supervisor, lab director or project manager.*

6.16 If the sample is dark and viscous, an auto-vial can be employed to remove particulate material. This is particularly evident in heavily contaminated petroleum samples. Reduce the sample to <10mL. Remove it from the blow-down apparatus with an appropriate size syringe. Pass it through the auto-vial back into the blow-down apparatus. The extract may concentrate more easily with the particulate matter removed. However, do not force the concentration as this may jeopardize the surrogate and target compound recoveries.

6.17 In some instances with heavily contaminated petroleum samples, it is possible to perform an extra step of hexane exchange to remove the asphaltene material that precipitates out in hexane. This decision should be made with the supervisor's approval. It may preserve the integrity of the target analytes and surrogates in the sample. This extract can also be auto-vialed to further remove any unwanted particulate materials.

6.18 *Turbo-Vap Concentration*: Place the TurboVap tube in the unit at a pressure of 20 PSI and a temperature of 44°C in the sensor mode of operation and reduce the extract to the final volume required before cleanup (refer to Table 1).

6.19 The sample may now undergo any necessary or required cleanups.

7. Percent Moisture Determination and Percent Lipid Determination

7.1 See the WHG SOP for *% Solids, Total Solids, Volatile Solids and % Lipids.*

8. Quality Control

8.1 Method Blank - A method blank must be extracted with every batch of samples (extract one for every twenty samples, if a large numbers of samples are to be processed). It consists of Diatomaceous earth and Ottawa sand spiked with 1mL (or the project-specified volume) of the appropriate surrogate solution. This extraction will demonstrate any background contamination associated with the extraction batch. Method blanks should not contain any analyte at a concentration greater than the reporting limit, or limits defined in the analysis SOP(s). Exceptions may be made for common laboratory contaminants, such as phthalates, however, any contact with plastics should be avoided. Recovery of surrogates must meet the specified limits.

8.2 Laboratory Control Samples (LCS) - A Laboratory Control Sample is extracted and analyzed with each batch of samples (extract one for every twenty samples, if a large numbers of samples are to be processed). The LCS is a blank spiked with the LCS spike mix and the surrogate mix for the particular test being evaluated.

8.3 Sample Surrogate Recoveries - Recoveries are monitored to evaluate the method performance. If recovery criteria are not met, data should be closely evaluated to determine if laboratory error or matrix effects are the cause. A repeat analysis and/or extraction is recommended to verify recoveries outside of control limits. If it is the judgment of the analyst in consultation with the QA Manager and the project manager, that the recovery is due to matrix interferences, the data may be reported with the surrogate results flagged in the final report.

8.4 Matrix Spikes - Extracted and analyzed at the frequency of a pair (Matrix Spike/Matrix Spike Duplicate (MS/MSD) per 20 samples. Recovery and % RPD are calculated and evaluated against established control limits. The Matrix Spike compounds should be representative of the compounds being investigated.

8.5 Sample Duplicates - Duplicates analyses can be performed on samples to demonstrate reproducibility. In some instances where a sample is known to contain significant concentrations of target compounds a sample duplicate may be extracted and analyzed in place of a matrix spike duplicate. Evaluate the %RPD of the sample and duplicate (or MS/MSD) against the established control limits.

8.6 If recoveries are not within limits, the following action is required: Check to be sure there are no errors in calculations, matrix spike solution and internals standards. Re-calculate the data and/or re-analyze the extract if any of the above checks reveal a problem. If the checks reveal no errors, and recovery of the LCS is within limits for these compound(s), then recovery problems encountered with the spiked sample are judged to be matrix- rather than system- related and the client should be informed of this via narrative in the final report.

8.7 Standard reference materials (SRM) are available from NIST to be extracted and analyzed with samples on a project specific basis. These are not used as controls but to evaluate potential matrix effects in associated samples. Advisory criteria: **a.** ± 35% of the accepted value for 80% of the certified results greater than five times the reporting limit. **b.** Mean %D ≤ 30% across all certified results greater than five times the reporting limit.

8.8 Tissue and sediment samples and some other project specific matrices can be preserved as frozen samples. Subsamples can be taken and the sample returned to the freezer for archiving.

8.9 Sample extracts in most cases are split before any cleanups are performed. The uncleaned extract is usually in a 4-mL Teflon-capped vial and placed in a freezer.

Table 1

Method	Exchange Solvent for Cleanup	Exchange Solvent for Analysis	Volume before Cleanup (mL)	Volume for Analysis (mL)
8081	DCM	Hexane	10.0	2.0
8082	DCM	Hexane	10.0	2.0
8270	None	None[a]	4.0	1.0
PAH[b]	None	None[a]	4.0	1.0
TPH	None	None[a]	N/A	1.0
EPH	Hexane	None	1.0	1.0

a- Hexane exchange to remove asphaltenes.
b- Including Alkylated PAHs

Note: Final Volumes before cleanup, and for analysis, can change based on project specific specs.

APPENDIX A-85—STANDARD OPERATING PROCEDURE FOR DETERMINATION OF PCBS (HOMOLOGUES) AND INDIVIDUAL CONGENERS BY GC/MS SIM

METHOD 680

Determination of PCBs (Homologues)
and Individual Congeners
By GC/MS SIM

1. Method Reference

1.1. Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio; November 1985.

2. Scope and Application

2.1. This method is applicable to the quantification of PCBs as homologs and/or congeners in water, soil, sediment and tissue using GC/MS in Selected Ion Monitoring mode, SIM. PCBs are identified and measured as isomer groups, i.e. by level of chlorination.

2.2. The sample preparation methods described herein are: 3510C, 3520C, 3545, and 3550B from the above reference.

2.3. The individual target compounds and homologue group compounds are found in Table C.

3. Summary of Method

3.1. Aqueous samples are serially extracted with methylene chloride in a 2 Liter Separatory Funnel at the required pH or on the Liquid Liquid Extractor (LLE). Soil samples are extracted by Sonication in a 1:1 methylene chloride - acetone mixture or on the Dionex Accelerated Solvent Extractor in methylene chloride. The extract is dried and exchanged to Hexane during concentration to a one milliliter (1mL) final volume or less in preparation for analysis. The extract maybe cleanup up with sulfuric acid, GPC, amino-propy or alumina columns. The extract is analyzed on a gas chromatograph, which is fitted with a narrow bore capillary column. The target analytes are resolved on the column and detected using a Mass Selective Detector (MSD). Concentrations are calculated from the MSD response using internal standard techniques.

	Approval Signatures	
Laboratory Director	for PTK	Date: 4/5/99
Section Supervisor		Date: 4/5/99
Quality Assurance Manager		Date: 4/5/99

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4. Sample Handling and Preservation

4.1. Water samples are collected in pre-cleaned 1-L amber glass bottle with a Teflon lined screw cap. Approximately one liter of sample is required for the analysis. Soil samples are collected in a pre-cleaned 250 mL glass jar with Teflon lined screw cap. Approximately 100 grams of soil is required for the analysis although more may be collected to provide a representative sample.

4.2. Samples should be preserved by cooling to 4°C and should remain at this temperature until extraction. No chemical preservative is required, and may interfere with the analysis.

4.3. Holding Times: Water samples should be extracted within 7 days of collection. Soil samples should be extracted within 14 days of collection. Sample extracts should be analyzed within 40 days of sample preparation.

5. General Points

5.1. Phthalate esters can be a major source of contamination if any material containing plasticizers (phthalates) comes in contact with the sample during the extraction process. Use of plastic or any material containing plasticizers (phthalates) should be avoided during extraction or analysis.

5.2. When emulsions are formed during the Separatory Funnel extraction process, centrifuging the extract may be necessary to break down the emulsion before continuing the serial extractions. If water does filter into the collected extract, the extract should be refiltered through sodium sulfate before the extract is concentrated to its final volume.

5.3. The injection port of the gas chromatograph can become contaminated with high boiling compounds resulting in the loss of sensitivity or breakdown of DDT to DDE and DDD in check standards. It may be necessary to replace the injection port liner and/or the silanized glass wool routinely to prevent this loss of sensitivity. Clipping off approximately four inches of the column at the injection end will also facilitate removing active sites in the injection port. Low instrument response can be detected during the daily tuning procedure by including pentachlorophenol and benzidine in the daily tuning mix.

5.4 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences or carryover. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed.

5.5 To minimize interferences, all glassware should be meticulously cleaned with detergent and hot water. After drying, bake glassware in an oven at approximately 450°C.

6. Equipment and Reagents

6.1. Glassware - Separatory funnel, 2 L with Teflon or glass stopper; Erlenmeyer flask 500 mL; graduated cylinder, 1 L; glass funnel; Kuderna-Danish (KD) evaporator; 10 mL concentrator tube.

6.2 Liquid Liquid Extractor- 500 mL flat bottom flasks; 1 L graduated cylinder; heating units.

6.3. Dionex ASE 200 Accelerated Solvent Extractor

6.4. Sample Concentrator - Apparatus for reducing prepared sample extract volumes (KD Bath or S-Evap or N-Evap Analytical Evaporator)

6.5. Gas chromatograph – Programmable, heating range from 40°C to 350°C; splitless-type inlet system, (Hewlett Packard 6890 or similar); mass selective detector (Hewlett Packard 5973 or similar); automatic injector (Hewlett Packard 6890 or similar).

6.6. Chromatography Column - Fused silica capillary column, 0.25mm ID x 30m length, 0.25µm film thickness (RTX-5, Restek Corporation, 5% diphenyl-95% dimethyl polysiloxane) or equivalent.

6.7. Data Acquisition System - Computerized system for collecting, storing, and processing detector output (Hewlett Packard Enviroquant target software) or equivalent.

6.8. Gases - Ultra high purity helium (99.9995%); Compressed nitrogen for N-Evap.

6.9. Supplies- glass wool; pH paper; boiling chips; sodium sulfate; funnels; 2-mL capacity glass vials; Syringes- 1mL, 0.5mL, 10 uL; and 1mL Teflon/silicone septa screw cap vials.

6.10. Reagents

6.10.1 Methylene Chloride - HPLC grade or better. Doe & Ingalls reserved lot(s).

6.10.2 Acetone - HPLC grade or better. Doe & Ingalls reserved lot(s).

6.10.3 Hexane- Pesticide quality or equavlent (Fisher Scientific).

6.10.4 Soil Sample Extraction Solvent - Prepared by mixing acetone and methylene chloride 50:50 by volume.

6.10.5 Sodium sulfate ($Na_2 SO_4$) - Granular, dried at 400°C for 4 hours. J.T.Baker 3375-15, or equivalent.

6.10.6 Diatomaceous earth - Purified by drying at 400°C for 4 hours, or extraction with methylene chloride to remove interferences.

6.11 Analytical Standards

Standards should be stored at -10°C or less, away from light when not in use. They should be discarded after 1 year unless the vendor expiration date states otherwise or if breakdown is observed. The daily calibration standard solution should be stored at 4°C and re-prepared every six months, or sooner if degredation is observed.

6.11.1 Surrogates – two surrogates are used, Dibromofluorobiphenyl (DBOB) and BZ 198. The concentrations of the surrogates in the final extracts should be at 1 ug/mL.

To prepare the surrogate spiking solution mix: For DBOB, add 200 uL of the 5000 ug/mL stock standard to 10 ml of acetone for 100 ug/mL solution. The BZ 198 stock comes at 100 ug/mL. Add 1 mL of each surrogate (DBOB and BZ 198 now both at 100 ug/mL) to 100 mL of acetone, for a 1 ug/mL final concentration, and a 100 mL final volume.

6.11.2 Stock Calibration Mix Standards are pre-made commercially available solutions from a variety of vendors. The solution is at multilevels for the PCB isomer for each homologue group. The stock solution concentration is 50 to 250ug/mL. With increasing degree of chlorination, there is an observed decrease of sensitivity on the mass spectrometer.

Preparation of the high level standard (5 to 25 ug/mL) to one 10 mL stock solution is as follows:

PCB Congener	Isomer Group	Stock Conc. ug/mL
BZ 1	Cl1	5 ug/mL
BZ 5	Cl2	5 ug/mL
BZ 29	Cl3	5 ug/mL
BZ 50	Cl4	10 ug/mL
BZ 87	Cl5	10 ug/mL
BZ 154	Cl6	10 ug/mL
BZ 188	Cl7	15 ug/mL
BZ 200	Cl8	15 ug/mL
BZ 209	Cl 9 and 10	25 ug/mL
BZ 77	Cl4	10 ug/mL
BZ 81	Cl4	10 ug/mL
BZ 105	Cl5	10 ug/mL
BZ 114	Cl5	10 ug/mL
BZ 118	Cl5	10 ug/mL
BZ 123	Cl5	10 ug/mL
BZ 126	Cl5	10 ug/mL
BZ 156	Cl6	10 ug/mL
BZ 157	Cl6	10 ug/mL
BZ 167	Cl6	10 ug/mL
BZ 169	Cl6	10 ug/mL
BZ 189	Cl7	10 ug/mL

Note: Any of the above congeners, may be reported as individual congeners, as well as within a homologue group. Also, the method is not limited to this congener list. Additional congeners may be analyzed via this method by utilizeing the MDL and PQL from a congener of the same homologue class.

Retention Time Congeners

Parameter	Isomer Group	Concentration ug/mL
BZ 77	Cl4	10
BZ 104	Cl5	10
BZ 208	Cl9	20

Stock solution

Parameter	Initial Conc	Volume added	Final Conc	Final volume (hexane)
PCB from vendor	50-250 ug/mL	1mL	5-25 ug/mL	10 mL
PCB Rt Time mix	100-200 ug/mL	1 mL	10-20 ug/mL	10 mL
4,4'-DDT	100 ug/mL	1 mL	10 ug/mL	10 mL
Gamma BHC	100 ug/mL	1 mL	10 ug/mL	10 mL

6 Level Curve Preparation for Individual Components (Minimum 5 Levels)

Calibration Level		Volume of High Std Added	Volume of Hexane added
Level 1	0.01-0.05 ug/mL	2 *uL*	998 *uL*
Level 2	0.1-0.5 ug/mL	20 *uL*	980 *uL*
Level 3	0.5-2.5 ug/mL	100 *uL*	900 *uL*
Level 4	1-5 ug/mL	200 *uL*	800 *uL*
Level 5	2-10 ug/mL	400 *uL*	600 *uL*
Level 6	5-25 ug/mL	1ml (stock solution)	none

Note: 20 uL of an Internal Standard is added to each standard level.

6.11.3 Matrix Spiking Solutions - Commercially obtained containing the nine congeners. To prepare the spiking solution, add 1mL of each solution to a 50mL volumetric flask and bring it to volume. 1mL of this solution is spiked into each Matrix Spike, Matrix Spike Duplicate and LCS (Laboratory Control Sample) sample. The final concentration in a 1mL extract will be 1-5 ug/mL for the congeners.

6.11.4 The Reference Standard solution is purchased from another source than the standards used to calibrate the instrument.

6.11.5 All samples and standards are spiked with the Internal Standards (IS) before analysis. The IS is intended to be used for both quantitation and the establishment of relative retention times. The mix can be commercially obtained from Chem Service at 750 ug/mL. 0.5 mL of the stock solution is added to 10 mL of hexane @37.5 ug/mL. 20 uL of the solution is spiked into 1mL sample and standard ampules. The final concentration on column is 0.75 ug/mL. The two IS's are Phenanthrene-d8 and Chrysene-d12.

7. Sample Preparation

7.1. Water Samples-Separatory Funnel (Method 3510C modified)

7.1.1 A one Liter water sample is measured in a graduated cylinder. The actual volume of the sample being extracted is recorded in the extraction bench logbook. This sample is poured into a separatory funnel.

7.1.2 The pH of the sample is determined by dipping a pasture pipette into the separatory funnel and transferring a drop of sample onto a strip of universal pH paper. Record this data on the extraction sheet.

7.1.3 Add 60 mL of methylene chloride to the separatory funnel and spike the sample with 1mL of the Surrogate solution. If sample requires Matrix Spike, also add 1mL of the Matrix Spike solution.

7.1.4 Seal and shake the separatory funnel vigorously for 1 to 2 minutes with periodic venting of the funnel into a hood. Note: the system should be vented immediately after the initial shaking to avoid pressure build up.

7.1.5 Place funnel in a rack and allow the water and the organic layers to separate for a minimum of 10 minutes after shaking. If an emulsion forms which is greater than one third the size of the organic layer then it must be broken up before continuing. Several procedures can be employed to do this.

7.1.5.1 The emulsion can be broken up using a glass rod in a mixing motion causing the bubbles to break up. The solvent layer is then drained into a flask or Turbovap tube.

7.1.5.2 The organic layer can be drained into a centrifuge cup and spun for several minutes. The non-emulsified organic layer is saved and the emulsion returned to the separatory funnel.

7.1.5.3 The emulsion can be filtered through a funnel with a glass wool plug topped with dried sodium sulfate.

7.1.5.4 If the emulsion cannot be broken (recovery of <80% of the methylene chloride, corrected for the water solubility if methylene chloride), transfer sample, solvent, and emulsion into the extraction chamber of a continuous extractor and go to Section 7.2.

7.1.6 The organic layer in all cases is filtered into a 250 mL Erlenmeyer flask or a TurboVap tube through a glass funnel packed with 20 grams of sodium sulfate in a filter paper cone or on a glass wool plug. The sodium sulfate filtration can be performed for each successive separatory funnel shake or at the end one time for the entire extract.

7.1.7 Repeat the rinse and shake steps two more times using a fresh portion of 60 mL of methylene chloride each time.

7.2 Water Samples-Liquid-Liquid Extraction (Method 3520C modified).

7.2.1 400 milliliters of methylene chloride is added to the LLE extractor, witch has a 500mL flatbottom flask attached. A water sample is measured in a 1 L graduated cylinder, and added to the methylene chloride. Sample volume is recorded in the extraction logbook.

7.2.2 The pH of the sample is determined by dipping a pasture pipette in to the LLE and transferring a drop to pH paper.

7.2.3 Add 1mL of the required Surrogate to each sample, blank and QC, and any other required spiking solution.

7.2.4 Turn on cool flow units. Turn on all heating units to a setting of four. Let LLE's extract for 18 to 24 hours.

7.2.5 Turn off heating units, let samples cool . Filter samples through sodium sulfate in a funnel with a glass wool plug. Samples will be filtered into KD flasks, then concentrated as outlined in Section 7.4.

7.2.6 The sample should be concentrated as outlined in Section 7.5.

7.3. Soil/Sediment Samples (Method 3545)

7.3.1. Weigh approximately 20 g of sample into beaker, record the actual weight used in the extraction bench logbook, add sufficient diatomaceous earth until dry, mix well, grind if necessary to obtain a free flowing powder. For Method Blanks and Laboratory Control Samples (LCS), aliquot approximately 20g infusorial/diatomaceous earth (use a representative sample weight for determining concentrations in blanks).

7.3.2. Use a prepared cell, cleaned by washing with soap and water between each use, and rinsed three times with extraction solvent (methylene chloride) immediately prior to use.

7.3.3. Close bottom end of cell, insert cellulose filter and use rod to press into place at the bottom of the cell. Make sure filter is properly seated.

7.3.4. Transfer entire contents of beaker to a 33mL cleaned stainless steel extraction cell. Record Sample IDs and associated Cell numbers in the ASE logbook. Do not attach labels to the outside of the cell. Labels may cause misalignment in the system or label may be damaged since the entire cell is placed in the oven during extraction.

7.3.5. Spike each cell with 1mL of the Surrogate mix and any appropriate Matrix/LCS spike.

7.3.6. Insert another cellulose filter and use rod to lightly press into place on top of sample. Close the top of the cell. Caps should be handtightened only. Clean rod between each sample.

7.3.7. Verify white O-rings are in place and in good condition on the ends of the cell.

7.3.8. Place extraction cells into the autosampler tray. Record autosampler position for each sample in the ASE logbook.

7.3.9. Load the collection tray with the appropriate number (up to 24) of 60-mL precleaned, capped vials with septa, labeled with corresponding sample IDs. Labels should only be placed from 1 3/8" to 3 1/8" from the top of the closed cap of the vial, to prevent blocking of the sensors on the system.

7.3.10. Select correct method on the system keypad and press start.

7.3.11. ASE 200 Conditions:

System Pressure:	14 MPa (2000 psi)
Oven Temperature:	100°C
Oven heat-up Time:	5 min.
Static Time:	5 min.
Solvent:	Methylene chloride
Flush Volume:	60% of extraction cell volume
Nitrogen Purge:	1 MPa (150 psi) for 60 seconds
Rinse Cycle	8 mL

7.3.12 The sample should be transferred to the proper glassware and concentrated as outlined in Section 7.5.

7.4. Soil Samples (Method 3550B)

7.4.1 Examine sample and decant any standing water and discard any stick or foreign objects. Weigh a 30g aliquot of a well-mixed sample into a solvent rinsed beaker. Record the actual weight used in the extraction bench logbook. A smaller amount may be added if it is known that the sample concentration is high. If the sample contains a water layer on top, decant the water before stirring.

7.4.2. Add sodium sulfate incrementally to the sample and mix until the sample is "powdery".

7.4.3. Add 100 mL (or more if necessary to cover the sample) of soil sample extraction solvent (acetone and methylene chloride [50:50]) and add 1mL of the Surrogate spike solution to all samples, blanks, matrix spikes, and matrix spike duplicates.

7.4.3.1 1mL of the Matrix Spiking solution should be added to the matrix spikes and matrix spike duplicates performed with each batch of samples.

7.4.3.2 Place the tip of the sonic disrupter into the sample - 1/2 inch below the solvent layer but above the sediment layer. Note: Rinse the tip with methylene chloride before placing it into the sample to prevent contamination.

7.4.4 Sonicate the sample for 3 minutes at a setting of at least 300 watts on Pulse mode. The analyst should observe very active mixing of the sample and solvent when the ultrasonic pulse is activated.

7.4.5 Transfer the solvent by decanting into a KD flask/concentrator tube with a funnel fitted with glass wool and sodium sulfate for drying the sample.

7.4.6 Repeat the extraction steps twice more with fresh 100mL portions of the soil extraction solvent (or enough to cover the sample).

7.4.7 The extract is now ready for concentration. If particles are present, filter the extract using Whatman No. 41 paper, centrifuge, or autovial prior to concentration.

7.5. Extract Concentration -Any of the above prepared extracts are concentrated as described here.

7.5.1 K-D Concentration:

Place the KD flask on the KD bath with boiling chips. The bath temperature should be 80-85°C. Macro-concentrate the sample to less than 10mL. This will take approximately 15-20 minutes. As an alternative the S-EVAP may be used to concentrate.

Transfer the 10mL concentrator tube to the N-Evap unit and bring the extract to a final volume of 1mL. If the sample appears extremely viscous and reduces in volume very slowly then a final volume of 5 or 10mL should be used to salvage any surrogate data. The solvent should be exchanged to hexane before acid cleanup is to be performed at the 1 mL volume.

7.5.2 Turbo-Vap Concentration:

Place the TurboVap tube in the unit at a pressure of 20 PSI and a temperature of 44°C in the sensor mode of operation and reduce the extract to a final volume of 1mL and exchange to hexane before acid cleanup.

The sample may now undergo any necessary or required cleanups.

8.0 Instrument Setup & Calibration

The instrument used for the analysis is a HP 5890A Series II or 6890 gas chromatograph. The HP system is equipped with a splitless injector, 7673-type autosampler. The mass spectrometer is a HP 5971A or 5973 with the HP Enviroquant data system.

8.1 The basic GC parameters are as follows:

Injector A Temp	300°C
Equil. Time	0-2 minutes
Oven Temp	45°C
Initial Value	45°C
Initial Time	1 minute
Rate	20°/minute
Final Value	150°C
Hold	1 min
Rate	10°/minute
Final Temp	310°C
Final Time	1.75 minutes
Purge/Valve A ON	0.8 minutes

8.2. Calibration

8.2.1 Before the analytical standards are analyzed the mass spectrometer must be adjusted to meet the proper ion criteria for DFTPP. This is demonstrated by injecting into the GC/MS system 1 uL of a 10 ug/mL DFTPP solution. To aid in further evaluating the analytical system the solution also contains Benzidine and Pentachlorophenol. The response of these two components when monitored on a daily basis will indicate the efficiency of the chromatography system. Benzidine and Pentachlorophenol should be present at their normal responses and no peak tailing should be visible. The following DFTPP mass intensity criteria should be used.

DFTPP KEY MASSES AND ABUNDANCE CRITERIA

Mass	m/z Abundance criteria
51	30-60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40-60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5-9 percent of mass 198.
275	10-30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17-23 percent of mass 442.

Tune acceptance should be verified at the beginning of every 12 hour analytical shift. The DFTPP may be combined with the calibration verification standard as long as both tuning and calibration acceptance criteria are met.

8.2.2 After the DFTPP passes criteria, the multi-level calibration standards listed in Section 6.11.2 are analyzed, from low concentration to high. A minimum of five calibration levels are analyzed.

The standards are reduced by the search software of the Enviroquant data system. Once all the components are identified, a linear curve is calculated for the components. The criteria for evaluation are as follows:

- The %RSD for each isomer in the ICAL should be less than 25 %
- Baseline separation of BZ 87 from BZ 154 & BZ 77.
- The signal to noise ratio must be ≥ 5 for m/z 499 of BZ 209, and for m/z 241 of chrysene –d12.
- The adundance of m/z 500 relative to m/z 498 for congener BZ 209 must between 70% – 95 %.
- A linear regression model may be employed, provided that the coefficient of determination (COD or r^2) is ≥ 0.99. Otherwise, construct a nonlinear calibration of no more than a third order equation. Statistical considerations in developing a non-linear calibration model require more data than the more traditional linear approach. A quadratic (second order) model requires six standards, and a third order polynomial requires seven standards. In setting model parameters, do not force the line through the origin. The COD or r^2 must be greater than or equal to 0.99. The analyst should select the regression order which introduces the least calibration error into the quantitation.
- The relative retention time of each compound in each calibration standard should agree within 0.06 RRT units.

8.2.2.1 If the curve does not meet criteria, the analyst should check the calculation of the standard preparation that was performed. If the problem appears to be isolated to a single calibration standard, that standard may be reanalyzed and the %RSD may be recalculated. If chromatographic problems are indicated by the standard chromatograms already analyzed, then the injection port should be serviced. This consists of cutting 6 to 12 inches off of the injector end of the column, changing the liner, glass wool and the septa. If the system shows poor sensitivity after this cleaning, the source may be cleaned. If this does not resolve the problem the column should be replaced and curves re-analyzed. Note: If the column is clipped be sure to adjust the SIMs windows.

8.2.3 Daily calibration - On a daily basis after the DFTPP has passed, a mid-level continuing calibration standard which contains all of the analytes of interest is analyzed. The criteria for acceptance are:

- The areas for mass 188 in phenanthrene-d10 and mass 240 in chrysene-d12 should not have degraded more than 30% from the previous claibration standard analyzed, or more than 50% from the initial calibration.
- The percent difference (or percent drift, %D) of all the congeners must be with 25% of the initial calibration for the Response Factors.
- The retention times of BZ 77 and BZ 104 should not vary by more than 10 seconds from one analysis to the next.
- The retention time of the internal standards must be within 30 seconds of the previous daily standard.
- A closing continuing calibration standard is suggested to ensure the analytical system is operating well at the end of a 12 hour tune run.

8.2.4 Reference standards from a separate source or different lot are analyzed after every initial calibration for evaluation against calibration standard solutions. % Difference should not be greater than ±15%.

9. Sample Analysis and Evaluation

Once a successful continuing calibration has been attained samples can be analyzed. The window for sample analysis is up to 12 hours after the DFTPP.

9.1 2 uL of sample extract is injected on the column. The IS is manually added (20 uL of 37.5 ug/mL solution) just before samples go onto the system. A dilution may be necessary to provide results that are within the calibration range.

9.1.1 Dilutions of sample extracts may be performed before or after addition of the internal standard. However if dilution is performed after the internal standard has been added is necessary to add additional IS in order to provide a concentration of 0.75 ug/mL for analysis.

9.2 The internal standards in the samples should remain at constant area counts with respect to the continuing calibration analyzed at the beginning of the run. The criteria for acceptance of the IS areas is –50% to +100% for all IS's. The IS retention times should not differ more than 30 seconds. Additionally, for chrysene-d12, the abundance of mass 241 relative to mass 240 should be ≥15%, and ≤ 25%. For phenanthrene-d10, the abundance of mass 189 relative to mass 188 should be ≥10%, and ≤ 22%.

9.3 Surrogates should fall within defined control limits for monitoring the sample extraction efficiency. Any anomalous conditions such as emulsions should be noted during the extraction. These conditions often are the cause of poor surrogate recoveries. If the sample did exhibit matrix effects during the extraction no corrective action is required, otherwise reanalyze and if necessary reextract. Surrogate control limits are listed in Table A.

9.4 For the PCB homologues, the quantitation ion and the confirmation ion maxima must fall within ± 1 scan.

9.5 In each PCB homologue group, the ratio of the quantitation ion area to the confirmation ion area must be within the acceptance ratios in Table C for a candidate peak to be accepted as present in a cluster. Also, at least one ion from the $(M-70)^+$ ion cluster must be present.

9.6 The five ion sets (retention windows) used in this method are:
Begin acquisition:

- From before BZ 1 to before BZ 104 (first Cl5).
- End the second window 10 seconds after BZ 77(last Cl4).
- End the thrid window 10 seconds after the 4,4'-DDT.
- End the forth window 10 seconds before BZ 208(first Cl9).
- The fifth window goes from BZ 208 till the end of the run.

10 Qualitative analysis

10.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are idefined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds are identified when the following criteria are met.

10.2 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound specific retention time will be accepted as meeting this criterion.

10.3 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

10.4 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

10.5 Each homologue group is examined for interference from other homologue groups that may co-elute with the compound of interest. The interference ions for each homologue are listed in Table C. If there is interference the areas must be adjusted to compensate.

11 Quantitative analysis

11.1 Once a compound has been identified in accordance with section 9.4 and 9.5, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP, (Extracted Ion Current Profile).

11.2 The sum of all the areas of a particular homologue must be obtained. This area is used in conjunction with the RF from the initial calibration for that homologue group, to generate the raw quantitaion value.

11.3 There is the potential co-elution of particular congeners that will interfer with the the quantititation of homologue groups. The area of the interfering ions must be accounted for within the homologue group being measured. This interference comes from a heavier molecular weight congener such as a heptachlorobiphenyl co-eluting with a low molecular weight congener like pentachlorobiphenyl. The fragmentation ions from the heptachlorobiphenyl ion are measured, and a correction factor is applied.

11.4 Example for co-elutions for isomers with two additonal chlorines: If a Cl7 isomer co-elutes with a Cl5 when quantifing the pentachlorobiphenyl homologues, a m/z 322 ion (the interference check ion for Cl7) from Cl7 $(M-70)^+$ isomer will be present at significant area counts in the Cl5 ion cluster. The area of the Cl5 quant and confirmation ion must be adjusted for the addition of the Cl7 area for qualitative identification and before quantiation can be performed. Thus the area from m/z 322 is multipled by the correction factor of 164% (from Table E) and subtracted from the area of m/z 324 to produce a corrected confirmation ion area for the Cl5 congener. The m/z 322 area is then multiplied by 108% and subtracted from the 326 quant ion for a corrected quant ion area for Cl5.

11.5 The total area for the Cl5 isomers is summed but is corrected for the contribution of Cl7 in 11.4. This corrected total area is used in calulations of the Cl5 homologue.

11.6 In some cases there will be a loss of an HCl from a Congener that can interfer with a lower molecular weight homologue group if there is co-elution. In these cases there is an odd $(M+35)^+$ ion. This is only an issue if there is a co-eluting isomer of a larger molecular weight PCB at high concentrations and a small amount of a lower chlorination isomer. To correct for the ^{13}C contribution, record the area for the $(M-1)^+$ from the cluster and multiply that area by 13.5%. Subtract this area from the area of the quantitation ion. The indicating interference ions are designated in Table F.

12. Calculations

12.1 Response factors and % RSD to evaluate Initial Calibration acceptablility.

Calculate RF by:

$$RF = \frac{area_{cmp}}{area_{is}} \times \frac{conc_{is}}{conc_{cmp}}$$

where:
area cmp = Area of the characteristic ion for the compound being measured.
area is = Area of the characteristic ion for the specific internal standard.
conc is = Concentration of the specific internal standard.
conc cmp = Concentration of the compound being measured.

Calculate % RSD by:

$$\%RSD = \frac{SD}{\bar{x}} \times 100 \qquad SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N-1}}$$

where:
% RSD = percent relative standard deviation
x = average of RF's
SD = standard deviation
xi = analytical results of each level in the final reporting units
N = number of results (levels)

12.2 Calibration Verification

12.2.1 %D to evaluate continuing calibration acceptabilty:

Calculate % Difference (%D) by:

$$\%D = \frac{\overline{RF}_i - RF_c}{\overline{RF}_i} \times 100$$

where: *RFi* - Initial Calibration average RF
RFc = Continuing Calibration RF

12.3 Results of Water Analysis- calculation as performed in report form:

$$\text{Concentration (ng/L)} = \frac{(Conc)\ (Vf)\ (DF) \times 1000}{(Vi)}$$

where:
Conc = Raw on-column concentration obtained from the quantitation report using Initial Calibration results (in ng/mL).
Vf = Final volume of extract (mL)
Vi = Volume of sample extracted (mL)
DF = Dilution factor, for manually prepared dilutions, not instrumental "dilutions".

12.4 Results of Sediment/Soil and Sludge Analysis- calculation as performed in report form:

$$\text{Concentration (ug/Kg)} = \frac{(Conc)\ (Vf)\ (DF)}{(W)\ (\%S)}$$

where:
Conc = Raw on-column concentration obtained from the quantitation report using Initial Calibration results (in ng/mL).
DF = Dilution factor, for manually prepared dilutions, not instrumental "dilutions".
Vf = Extract final volume (mL)
W = Aliquot of sample (wet), g
%S = Sample % solid (in decimal form)

13. Quality Control

13.1 Method Blank - A method blank must be extracted with every batch of samples extracted. It consists of reagent water or ottowa sand spiked with 1mL of the surrogate solution. This extraction will demonstrate the background contamination of the apparatus in the laboratory. Method blanks should not contain any analyte at a concentration greater than the reporting limit. Exceptions may be made for common laboratory contaminants of phthalate esters. Recovery of ALL surrogates must be within 50 to 125%.

13.2 Sample Surrogate Recoveries - Recoveries are monitored to evaluate the method performance. If recovery criteria (see Table A) are not met, data should be closely evaluated to determine if laboratory error or matrix effects are the cause. A repeat analysis and/or extraction is recommended to verify recoveries outside of control limits. If it is the judgment of the analyst with consultation, that the recovery is due to matrix interferences data may be reported with the surrogate results called out in the final report, and noted in the project narration.

13.3 Laboratory Control Samples (LCS) - A Laboratory Control Sample is extracted and analyzed with each batch of samples. The LCS is a blank spiked with 1mL of congener spike mix. Evaluate all compounds of interest against the acceptance limits listed in Table D.

13.4 Matrix Spikes - Extracted and analyzed at the frequency of a pair (Matrix Spike/Matrix Spike Duplicate (MS/MSD)) per 20 samples. Recovery and RPD are calculated and evaluated against control limits (see Table D). The matrix spike compounds should be representative of the compounds being investigated.

13.4.1 If recoveries are not within limits, the following action is required: Check to be sure there are no errors in calculations, matrix spike solution and internals standards. Re-calculate the data and/or re-analyze the extract if any of the above checks reveal a problem. If the checks reveal no errors and recovery of the LCS is within limits for the compound(s), the recovery problem encountered with the dosed sample is judged to be matrix- rather than system- related and the client should be informed of this via narrative in the final report.

13.5 Duplicates - Duplicates are typically in the form of a Matrix Spike or Blank Spike Duplicate. In some instances where a sample is known to contain significant concentrations of target compounds a sample duplicate may be extracted and analyzed in place of a matrix spike duplicate. Evaluate the %RPD of the MS/MSD against the acceptance criteria listed in Table D.

13.6 Method Performance

13.6.1 Method Detection Limit (MDL) studies must be performed annually or whenever significant changes occur to the instrumentation.

13.6.2 As a one-time demonstration of proficiency, IDP, every analyst must analyze four QC samples, and demonstrate precision and accuracy comparable to SW846 guidelines. Refer to the method reference for the specific procedure and criteria.

Table A: Surrogate Recovery Acceptance Criteria

Surrogate	Water %Recovery	Soil % Recovery
4,4'-Dibromo-Octafluoro biphenyl (DBOB)	50-125	50-125
BZ 198	50-125	50-125

Note: The above limits will be replaced by laboratory limits generated by QC charting, when available.

Table B: Internal Standard Compounds

Parameter	Concentration
Chrysene-d12	0.75 ug/mL
Phenanthrene-d10	0.75 ug/mL

Table C: Target Compounds and Quantitation Ions

Parameter	1^0 Ion	2^0 Ion	CASRN	Acceptance Ratio	M-70 Confirm. Ion	Interfer. Check Ion M+70	Interfer. Check Ion M+35
Monochlorobiphenyls	188	190	27323-18-8	2.5-3.5	152	256	222
Dichlorobiphenyls	222	224	25512-42-9	1.3-1.7	152	292	256
Trichlorobiphenyls	256	258	25323-68-6	0.8-1.2	186	326	290
Tetrachlorobiphenyls	292	290	26914-33-0	1.1-1.5	220	360	326
Pentachlorobiphenyls	326	324	25429-29-2	1.4-1.8	254	394	360
Hexachlorobiphenyls	360	362	26601-64-9	1.0-1.4	288	430	394
Heptachlorobiphenyls	394	396	28655-71-2	0.8-1.2	322	464	430
Octachlorobiphenyls	430	428	31472-83-0	0.9-1.3	356	498	464
Nonachlorobiphenyls	464	466	53742-07-7	1.1-1.5	390	---	498
Decachlorobiphenyl	498	500	2051-24-3	0.9-1.3	424	---	---
BZ 77	292	290	32598-13-3	1.1-1.5	220	360	326
BZ 81	292	290	70362-50-4	1.1-1.5	220	360	326
BZ 105	326	324	32598-14-4	1.4-1.8	254	394	360
BZ 114	326	324	74472-37-0	1.4-1.8	254	394	360
BZ 118	326	324	31508-0-6	1.4-1.8	254	394	360
BZ 123	326	324	65510-44-3	1.4-1.8	254	394	360
BZ 126	326	324	57465-28-8	1.4-1.8	254	394	360
BZ 156	360	362	38380-08-4	1.0-1.4	288	430	394
BZ 157	360	362	69782-90-7	1.0-1.4	288	430	394
BZ 167	360	362	52663-72-6	1.0-1.4	288	430	394
BZ 169	360	362	32774-16-6	1.0-1.4	288	430	394
BZ 189	394	396	39635-31-9	0.8-1.2	322	464	430

Table D: Matrix Spike and LCS Recovery Limits

Compound Name	Water Recovery Limits (%)	RPD	Soil Recovery Limits (%)	RPD
BZ 1	40-140	50	40-140	50
BZ 5	40-140	50	40-140	50
BZ 29	40-140	50	40-140	50
BZ 50	40-140	50	40-140	50
BZ 87	40-140	50	40-140	50
BZ 154	40-140	50	40-140	50
BZ 188	40-140	50	40-140	50
BZ 200	40-140	50	40-140	50
BZ 209	40-140	50	40-140	50

Note: The above limits will be replaced by laboratory limits generated by QC charting, when available.

Table E: Interference Ions for Two Additional Chlorines

% measured Ion for subtraction

Isomer Group	Quant Ion	Conf. Ion	Interfer. Ion	Quant Ion %	Confirm. Ion %
Trichlorobiphenyls	256	258	254	99	33
Tetrachlorbiphenyls	292	290	288	65	131
Pentachlorobiphenyls	326	324	322	108	164
Hexachlorobiphenyls	360	362	356	161	71
Heptachlorobiphenyls	394	396	390	225	123

Table F: Interference Ions for One Additional Chlorine

% measured Ion for subtraction

Isomer Group	Quant ion	Interference Ion	Quant Ion %
Dichlorobiphenyls	222	221	13.5
Trichlorobiphenyls	256	255	13.5
Tetrachlorbiphenyls	292	289	17.4
Pentachlorobiphenyls	326	323	22.0
Hexachlorobiphenyls	360	357	26.5
Heptachlorobiphenyls	394	391	30.9
Octachlorobiphenyls	430	425	40.0

APPENDIX A-86—STANDARD OPERATING PROCEDURE FOR TOTAL ORGANIC CARBON

Benchmark Analytics

TOTAL ORGANIC CARBON
SM# 18 5310 B

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BENCHMARK ANALYTICS
S.O.P. REVIEW LOG

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This document has been reviewed for errors and procedural discrepancies. No such errors or discrepancies have been found as of the last review date. All persons who have reviewed this document and the date of their review are listed below.

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1.0 Abstract

1.1 Discussion

The organic carbon in water and wastewater is composed of a variety of organic compounds in various oxidation states. Some of these carbon compounds can be oxidized further by biological or chemical processes, and the BOD or COD tests may be used to characterize these compounds. TOC is a more convenient and direct expression of total organic content. Unlike BOD and COD, TOC is independent of the oxidation of the organic matter. To determine the quantity of organically bound carbon, the organic molecules must be broken down to single carbon units and converted to a single molecular form that can be measured quantitatively.

This method includes the measurement of organic carbon in drinking, surface, and saline waters, domestic and industrial wastes. In this method TOC is determined by injecting a sample into a reaction chamber, packed with a catalyst and held at a fixed temperature. The organic carbon is converted to carbon dioxide by the action of the catalyst and the elevated temperature. The concentration of carbon dioxide generated is directly proportional to the concentration of organic carbon in the sample. Nitrogen is used as the carrier gas to transport the oxidized sample from the reaction chamber to a non-dispersive infrared analyzer sensitized to respond only to carbon dioxide. The concentration is displayed on the digital display meter. Since our analyzer measures total carbon which includes both organic and inorganic carbon, the inorganic portion must be eliminated. This is done by purging the sample under acidic conditions ($pH<2$) to convert the inorganic carbon to carbon dioxide by volatilization.

1.2 Safety

Lab coats, safety glasses and gloves should be worn at all times when handling unknown and wastewater samples.

2.0 Interferences

2.1 Carbonate and bicarbonate carbon represent an interference since they are not a part of the oxygen demand in a receiving stream. They must be removed or accounted for in the final calculation.

2.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter syringe. The opening of the syringe limits the maximum size of particles which may be included in the sample.

2.3 Sampling and storage of samples in glass bottles is preferable. Plastic bottles are acceptable if it is established that they do not contribute contaminating organics into the sample.

2.4 Because of the possibility of oxidation or bacterial decomposition of components, the lapse of time between collection and analysis should be kept to a minimum. Samples should also be kept cool (4°C) and protected from sunlight and atmospheric oxygen. In instances where analysis cannot be performed within 2 hours from the time of sampling, the sample is acidified ($pH \leq 2$) with HCl or H_2SO_4.

3.0 Apparatus

3.1 Ionics, Inc. Model 1555 Carbon Analyzer.

3.2 Nitrogen gas.

3.3 Syringe, 100 µL.

3.4 Stir plates.

3.5 Volumetric flasks, class A.

3.6 Beakers or Erlenmeyer flasks.

4.0 Solutions

4.1 Reagents

4.1.1 Reagent water - Milli-Q water.

4.1.2 85% Phosphoric Acid

4.2 Standards

4.2.1 Stock Carbon Standard, 1000 mg/l - Dissolve 2.128 g of anhydrous Potassium Hydrogen Phthalate, $C_8H_5KO_4$ in a 1000 mL volumetric flask in Milli-Q water. Dilute to the line and mix well.

4.2.2 Working Standards - Prepare the following standards from the stock standard into 50 mL volumetric flasks. Dilute to the line with Milli-Q water and mix well.

mLs stock standard	Final volume	Concentration mg/L
0	50	0
0.25	50	5
0.50	50	10
2.50	50	50
5.0	50	100

5.3 Sample Analysis

5.3.1 Prepare standards as in section 4.2.

5.3.2 All water samples must be purged of inorganic carbon in the following manner.

5.3.2.1 Pour 50 mL of sample into a beaker.

5.3.2.2 Add 10 drops of 85% Phosphoric Acid.

5.3.2.3 Add a stir bar and stir on a stir plate for 15 minutes.

5.3.2.4 Samples are now ready to inject.

5.3.3 Once the ready light is lit, inject 100 µL of sample starting with the standards. Remember to wait until the reading is stable before recording.

5.3.4 Each sample must be analyzed until the same reading is obtained twice.

6.0 Calculations

6.1 Use the programmable calculator to construct a linear calibration curve. The following calculations are based on Radio Shack calculator model EC-4024.

6.1.1 Clear the accumulators by pressing (shift) [KAC].

6.1.2 Enter the lowest concentration followed by [Xd,Yd].

6.1.3 Enter the corresponding absorbance followed by [DATA].

6.1.4 Repeat steps 6.1.2 and 6.1.3 for the remaining standards.

6.1.5 Press (shift) [r] to display the correlation.

6.1.6 To find the concentration, enter the absorbance followed by (shift) [x'].

6.1.7 To determine the sample concentration take the concentration from the curve and multiply by the dilution factor.

7.0 Quality Assurance/Quality Control

7.1 Analyze one method blank per run.

7.2 Analyze one laboratory control standard per run.

7.3 Analyze one duplicate per run or every 10 samples.

7.4 Analyze one calibration check per run or every 10 samples.

7.5 Analyze one spike per run or every 10 samples.

APPENDIX A-87

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF DISSOLVED GASES IN GROUNDWATER BY MODIFIED METHOD RSK-175

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF DISSOLVED GASES IN GROUNDWATER BY MODIFIED METHOD RSK-175

Applicable Matrix or Matrices: Water
Standard Compound List and Reporting Limits: See Table 1

Approvals and Signatures

Laboratory Director: Michael Wheeler, Ph.D. Date: 2/28/02

QA Manager: Kirstin McCracken Date: 2/28/02

Organics Technical Director: Bryce E. Stearns Date: 2/28/02

1.0 SCOPE AND APPLICATION

1.1 This document describes a procedure for the determination of dissolved gases in groundwater. The method is applicable to the preparation of water samples for the analysis of the headspace to quantify part-per-billion levels of dissolved gases in water samples.

2.0 SUMMARY OF METHOD

2.1 A water sample is collected in the field in a 44-mL VOA vial with no headspace. Prior to analysis the sample is transferred into a 22-mL serum vial with a crimp cap. Headspace is generated using UHP nitrogen. The sample is loaded onto the headspace autosampler and analyzed by Gas Chromatography (GC). The headspace is split in the GC injector to two columns, one equipped with a Flame Ionization Detector (FID), the other with a Thermal Conductivity Detector (TCD). Using similarly prepared calibration standards, the concentration of dissolved gas in the original sample can be determined.

3.0 DEFINITIONS

3.1 Calibration Standard (CAL) - Prepared from the stock standard. The CAL standards are used to calibrate the instrument response with respect to analyte concentration.

3.2 Continuing Calibration Verification (CCV) - An analytical standard containing all target analyte compounds that is used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.3 Method Blank (ABLK, similarly known as the LABORATORY REAGENT BLANK) - The method blank is the analysis of blank water to demonstrate that the analytical system is free of target compounds below their RL.

3.4 Laboratory Control Sample (LCS) - The LCS consists of a fortified aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. Hydrocarbon standards are from a source other than that used to calibrate the system. The TCD performance is validated with an injection of room air. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate measurements.

3.5 Initial Calibration Verification (ICV) - An analytical standard solution containing all target analytes that is prepared from a source external to the laboratory and independent from the source of the initial calibration standards. The purpose of the ICV is to verify that the initial calibration is in control.

4.0 INTERFERENCES

4.1 Target compound identification in any GC method is based on retention time data. False positive identifications may result from nontarget compounds with retention time windows similar to those of the target compounds.

4.2 Reagents and containers may introduce target and nontarget contaminants.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for materials or procedures known to be hazardous.

5.2 STL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in these methods. Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. STL also has a written environmental health and safety plan.

5.3 MSDS' should be reviewed for chemicals that have the potential to be highly toxic or hazardous

6.0 EQUIPMENT AND SUPPLIES

6.1 Sample Containers:

- 44mLVOA vials
- 22mL crimp cap vials

6.2 Instrumentation

- GC-FID-TCD- Varian 3600 with FID-TCD
- Column(FID) - Restek Rt-UPLOT; 30m, 0.53mm ID
- Column (TCD) - Alltech CTR I; 6ft.inner with porous polymer and 6ft. outer with molecular sieve
- Autosampler - Tekmar 7050 Headspace Autosampler

6.3 Syringes - 10μL - 5.0-mL gas tight syringes with Luer-Lok tip

6.4 Data System - Chrom Perfect or Multichrom for acquisition and Target™ for data processing.

7.0 REAGENTS AND STANDARDS

7.1 Gas cylinders of ultrahigh purity argon, helium, hydrogen, and nitrogen.

7.2 Calibration Standards: The primary standard is purchased through Scott Specialty Gases. The FID calibration standard is composed of nominally 1% (mole basis) methane, ethane, ethene, acetylene, and propane. The TCD calibration standard is composed of nominally 5% (mole basis) carbon dioxide.

7.3 The calibration levels are achieved by injecting different amounts of the standard into a 22-mL vial that contains 18 mL of deionized water and 4 mL of headspace.

7.4 Laboratory Control and Initial Calibration Verification Samples: The hydrocarbon LCS and ICV are fortified to the concentration of the middle calibration standard.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

8.1 Samples are collected in the field in a 44-mL VOA vial. The samples are preserved with 1:1 HCl to a pH of less than 2 **unless they are being analyzed for carbon dioxide**. Acid converts inorganic carbon to carbon dioxide. Care should be taken that no headspace is present when capping the vials. Samples are maintained at a temperature of 4°C and should be analyzed within 14 days of collection.

9.0 QUALITY CONTROL

9.1 Method Detection Limits - Method detection limits (MDLs) are determined annually in accordance with the method described in 40 CFR, Part 136, Appendix B.

9.2 Initial Calibration - A five-point calibration is performed. The RSD of the response factors for each analyte must be within 30%.

9.3 Initial Calibration Verification - An ICV must be analyzed run following the acquisition of the five-point initial calibration. The ICV is fortified to the concentration of the middle calibration standard. The calibration factor (CF) for the ICV must be within 30%D of that from the initial calibration.

9.4 Laboratory Control Sample - An LCS must be analyzed at the beginning of each 24-hour analytical batch. The hydrocarbon LCS is fortified to the concentration of the middle calibration standard. The resulting target compound concentration must meet the recovery criteria of 70-130%. The TCD performance is validated by analysis of 1 mL of room air (78.1% N2; 21.9% O2 on area percent basis).

9.5 Method Blank - One blank must be analyzed run with every batch of samples or 1 in every 20 samples, whichever is more frequent. The method blank is analyzed following the calibration standards.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Initial Calibration –Establish an initial calibration curve using the concentrations noted in the table below.

Compound	Cal Level 1	Cal Level 2	Cal Level 3	Cal Level 4	Cal Level 5
Volume Injected (uL)	1.3	50	200	600	1000
Methane	0.47	18	73	218	363
Ethane	0.89	34	136	409	681
Ethene	0.83	32	127	381	636
Acetylene	0.77	30	118	354	590
Carbon Dioxide	0.5%	2.5%	5%	7.5%	10%

Compound	Cal Level 1	Cal Level 2	Cal Level 3	Cal Level 4	Cal Level 5
Volume Injected (mL)	0.1	0.5	1	1.5	2
Carbon Dioxide	500	2500	5000	7500	10000

Concentrations are in µg/L unless noted otherwise.

- For each analyte, calculate the mean calibration factor from analyses of the calibration solutions.
- Calculate the standard deviation (SD) and relative standard deviation (RSD) from each mean.
- The %RSD average of all analytes must be ≤ 30%

10.2 Continuing Calibration Verification – Analyze a continuing calibration verification at the beginning of each 24-hr analytical window. The CCV is fortified to the concentration of the middle calibration level. The %D between the

CCV CF and the calibration average CF for each analyte must be less than or equal to 30%.

10.3 Laboratory Control Sample (LCS) – Analyze a LCS each 24-hour window following the CCV. The hydrocarbon LCS is fortified to the concentration of the middle calibration level. Calculate the percent recovery. The resulting target compound concentration must be between 70-130% of the expected value. TCD performance is evaluated by analysis of room air. The area percent (N2, O2) must fall within 70-130% of the room air concentrations (78.1 and 21.9 %, respectively).

10.4 Method Blank – Analyze the method blank following the completion of the CCV and LCS. Method blanks must result in target compound concentrations less than one-half the RL.

11.0 PROCEDURE

11.1 Sample Analysis (GC-FID) - Remove the samples from the refrigerator and allow to come to room temperature. Transfer the sample into a 22-mL vial with a crimp cap. Place the vial upside down in a three-finger clamp attached to a ring stand. Insert a 22-gauge needle into the septum. Using a 5-mL gastight syringe, inject 4 mL of UHP nitrogen into the sample. The helium forces out an equal amount of sample through the 22-gauge needle to create a headspace volume of 4 mL. Withdraw the needle and syringe from the vial and load the sample onto the Tekmar headspace autosampler. The autosampler allows the sample's water and headspace phases to equilibrate at 40°C. 100 µL of the sample headspace are injected directly onto the GC column where the target compounds, if present, are detected by FID. Acquire the data and process on Chrom Perfect or Multichrom. The instrument operating conditions are outlined below.

<u>GC Conditions</u>

Gas Flows:	
Carrier (Hydrogen):	30 mL/min
Oven Program:	40°C for 1.5 minutes

<u>FID Conditions</u>

FID Temp.:	200°C
Hydrogen Flow:	30 mL/min
Air Flow:	300 mL/min

11.2 Sample Analysis (GC-TCD) – Remove the samples from the refrigerator and allow to come to room temperature. Transfer the sample into a 22-mL vial with a crimp cap. Place the vial upside down in a three-finger clamp attached to a ring stand. Insert a 22-gauge needle into the septum and using a 5-mL gastight syringe, inject 4 mL of nitrogen into the sample. The nitrogen forces out an equal amount of sample through the 22-gauge needle to create a headspace volume of 4 mL. Withdraw the needle and syringe from the vial. Manually inject 1.0 mL of the sample is onto the GC column where the target compounds, if present, are detected by TCD. Acquire the data on MultiChrom and process on Target 3.1. The operating conditions are outlined below.

GC Conditions

Gas Flows:	
Carrier (Argon):	60 mL/min
Oven Program:	75°C for 3.5 minutes
TCD Temp.:	150°C
Filament Temp.:	185°C

12.0 CALCULATIONS

12.1 Calibration Factor for GC-FID-TCD

$$\mathbf{CF_{\chi} = A_{\chi}/C_{\chi}}$$

where:
CF_{χ} = Calibration factor of compound χ
A_{χ} = Peak area of compound χ in the calibration standard
C_{χ} = Concentration of compound χ in the calibration standard

12.2 Percent Difference for Calibration Factors

$$\mathbf{\%\ D = (CF_{ave} - CF_{c} / CF_{ave}) \times 100}$$

where:
CF_{ave} = Average CF for an analyte from the initial calibration
CF_{c} = CF for an analyte from current check standard

12.3 Relative Standard Deviation

$$\mathbf{\%RSD = (SD / CF_{ave}) \times 100}$$

where:
CF_{ave} = Average CF for an analyte from the initial calibration
SD = Standard Deviation of average CFs for a compound

12.4 Sample Concentration in water

$$\mathbf{C_\chi = (A_\chi/CF_{ave}) \times DF}$$

where:
C_χ = Concentration of target analyte χ in sample (ug/L)
A_χ = Peak area of analyte χ
CF_{ave} = Average calibration factor for an analyte from the calibration
DF = Dilution factor

12.5

13.0 METHOD PERFORMANCE

13.1 Method detection limits are calculated using the formula:

$$\mathbf{MDL = S\ t_{(n-1,\ 1\text{-alpha} = 0.99)}}$$

where:
n = number of replicates (minimum of 7)
S = the standard deviation of the replicate analyses
$t_{(n-1,\ 1\text{-alpha} = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.0 DATA ASSESSMENT AND CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Data assessment and acceptance criteria for out of control data are summarized in Table 2.

15.2 Corrective actions for out of control data are summarized in Table 2.

16.0 CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

16.1 Summarized in Table 2.

17.0 WASTE MANAGEMENT

17.1 The USEPA requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

18.0 REFERENCES

18.1 RSKSOP-175, Revision 0, August 11, 1994.

19.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION FORMS

Table 1. Analytes, CAS Numbers, and Reporting Limits (RL)

Analyte	CAS Numbers	RL (µg/L)
Methane	000074-82-8	2
Ethane	000074-84-0	4
Ethene	000074-85-1	3
Acetylene	000074-86-2	3
Carbon Dioxide	000124-38-9	350

Table 2: Quality Control Criteria & Corrective Action

Quality Control Criteria	Frequency	Acceptance	Corrective Action
ICAL	As Required	Average CF %RSD must be ≤ 30	System check, Recalibrate, Reanalyze
ICV	Following Initial Calibration Curve	Average CF %RSD must be ≤30	System check, Recalibrate, Reanalyze
CCV	Beginning of each 24 hour window	CF %Difference each Target Compound ≤30	System Check, Recalibrate
LCS	Following the CCV	70-130% Difference for each hydrocarbon compound; within 30% of N2/O2 for TCD air constituents	System Check, Recalibrate
Method Blank	Following each LCS or 1 every 20 samples	Targets < ½ Reporting Limits	Check for contamination, Reanalyze, correct as required
Samples	Per Request	Concentration must fall within the calibration range	A dilution is applied to the sample; the target concentration falls between the two high points of the calibration curve

Table 3: Compound Constants

Compound	Molecular Weight (g)
Methane	16
Ethane	30
Ethene	28
Acetylene	26
Carbon Dioxide	44

APPENDIX A-88

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF TRACE ELEMENTS BY ICP-MS

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF TRACE ELEMENTS BY ICP-MS

Approvals and Signatures

Laboratory Director: Michael F. Wheeler, Ph.D. Date: 9/23/02

QA Manager: Kirstin L. McCracken Date: 9/23/02

Inorganic Technical Director: Kristine A. Dusablon Date 9/23/02

Inorganic Supervisor: William S. Cicero Date 9/23/02

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of total/dissolved metals in groundwater, surface water, drinking water, wastewater, sludge and soil samples using inductively coupled-mass spectrometry (ICP-MS). This procedure is applicable to the elements listed in Table 1.

1.2 Instrument detection limits (IDLs), method detection limits (MDLs) and linear working ranges are dependent on sample matrix, instrumentation and operating conditions and are determined using the procedure and frequency prescribed in this SOP.

2.0 SUMMARY OF METHOD

2.1 A sample submitted for analysis is acid digested, nebulized and transported by argon gas to a plasma torch. The ions produced are introduced via direct interface into a mass spectrometer. Characteristic emission spectra are produced and sorted according to their mass-to-charge ratios, quantified using an electron multiplier and processed by a data handling system.

2.2 This procedure is based on EPA Method 200.8, SW-846 Method 6020 and CLP SOW ILM05.2.

3.0 DEFINITIONS

3.1 Accuracy: the degree of agreement between a measurement and the true or expected value, or between the average of a number of measurements and the true or expected value.

3.2 Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of a similar matrix, meeting the above mentioned criteria.

3.3 Calibration: the establishment of an analytical curve based on the absorbance, emission intensity or other measured characteristic of known standard.

3.4 Calibration Blank (ICB/CCB): a volume of reagent water acidified with the same acid matrix as in the calibration standards.

3.5 Calibration Standards: a series of known standard solutions used to calibrate the instrument response with respect to analyte concenteration.

3.6 Continuing Calibration Verification (CCV): a prepared standard solution used to verify the stability of the instrument calibration and instrument performance during the analysis of samples.

3.7 Corrective Action: action taken to eliminate the causes of an existing non-conformance, defect or other undesirable situation in order to prevent recurrence.

3.8 Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

3.9 Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

3.10 ICP-MS-A technique for the multi-element determination of elements in solution. The basis of the technique is the detection of atomic ions produced by an ICP and sorted by mass/charge ratio.

3.11 Inteference Check Solution (ICS): a solution of known concentrations of intefering elements that will demonstrate the magnitude of inteference and provide an adequate test for any corrections.

3.12 Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

3.13 Initial Calibration Verification (ICV): A prepared standard solution from a source separate from that of the calibration standards used to verify the concentration of the calibration standards and the adequacy of instrument calibration.

3.14 Instrument Detection Limit (IDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific instrument. The IDL is associated with the instrumental portion of a specific method only, and sample preparation steps are not considered in its derivation. The IDL is a statistical estimation at a specified confidence interval of the concentration at which the relative uncertainty is +100%. The IDL represents a range where qualitative detection occurs on a specific instrument. Quantitative results are not produced in this range.

3.15 Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

3.16 Linear Dynamic Range: The concentration range over which the instrument response remains linear.

3.17 Matrix: the substrate of a test sample.

3.18 Matrix Duplicate (MD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate; Laboratory Duplicate.

3.19 Matrix Spike (MS): field sample to which a known amount of target analyte(s) is added.

3.20 Matrix Spike Duplicate (MSD): a replicate matrix spike.

3.21 Method Blank: a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

3.22 Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which the relative uncertainty is +100%. The

MDL represents a range where qualitative detection occurs using a specific method. Quantitative results are not produced in this range.

3.23 Percent Solids (%S): the proportion of solid in a soil sample.

3.24 Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical and/or biological integrity of the sample.

3.25 Quality Control Sample: a control sample, generated at the laboratory or in the field, or obtained from an independent source, used to monitor a specific element in the sampling and/or testing process.

3.26 Serial Dilution: the dilution of a sample by a factor of five.

3.27 Tune: the analysis of a solution containing a range of isotope masses to establish ICP-MS accuracy, resolution and precision prior to calibration.

4.0 INTERFERENCES

4.1 Isobaric Elemental Interferences

Isobaric Elemental Interferences are caused by isotopes of different elements that form singly or doubly charged ions of the same nominal mass-to-charge ratio and cannot be resolved by the mass spectrometer. Correction for this interference is handled by the data system and is accomplished by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest.

4.2 Abundance Sensitivity

Abundance sensitivity is a property that defines the degree to which the wings of a mass peak contribute to adjacent masse. The abundance sensitivity is affected by ion energy and mass filter operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize occurrence.

4.3 Isobaric Polyatomic Ion Interference

Isobaric Polyatomic Ion Interference is caused by ions consisting of more than one atom, which have the same mass-to-charge ratio as the isotope of interest and cannot be resolved by the mass spectrometer. These interferences should be recognized, and when they cannot be avoided by the selection of alternative isotopes, appropriate corrections should be made to the data. Instrument operating parameters should be set to conditions that will minimize this phenomenon.

4.4 Physical Interference

Physical interferences such as a change in viscosity, surface tension and dissolved solids are known to affect instrument responses to certain samples. These physical effects can be reduced by dilution, matrix matching, as well as not allowing dissolved solids within the samples to exceed 0.2% (w/v).

4.5 Memory Interferences

Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. An active rinse monitoring cycle is employed by the software and will not allow the analysis of the next sample until levels drop below those of the determined baseline. The analytes chosen for this are B, Al, Ag, and Sb at masses 11, 27, 107, and 123, respectively. The minimum rinse time is set at 120 seconds. Memory interference can also be identified by monitoring the three replicate integrations that are used for data acquisition.

4.6 Polyatomic Interference

Nitric acid is preferred for ICP-MS in order to minimize polyatomic interferences known in the presence of the chloride ion. Hydrochloric acid is required to maintain stability in solutions containing antimony and silver. Corrections for chloride polyatomic interferences are applied to data regardless of whether hydrochloric acid is used in digestion, as the chloride ion is common in environmental samples.

5.0 SAFETY

5.1 The toxicity or carcinogenity of each chemical used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be minimized as reasonably possible. A reference file of Material Safety Data Sheets (MSDS) for this test method is available to all personnel and must be read prior to performing this procedure. All laboratory personnel must be familiar with the laboratory environmental health and safety plan described in the STL Corporate Safety Manual (CSM).

5.2 Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. These reagents should be used in a fume hood, whenever possible and if eye or skin contact occurs, immediately flush with large volumes of water. Protective clothing and eye shields should always be worn when working with these reagents.

5.3 The analytical plasma sources emit radiofrequency radiation and intense UV radiation. ICP plasma should only be viewed with proper eye protection from UV emissions.

5.4 Metal salts are extremely toxic if inhaled or swallowed. Hands must be washed thoroughly after handling.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively Coupled Plasma Mass Spectrometer: Capable of scanning a mass range of 5-240 amu with a minimum resolution capability of 0.9 amu peak width at 10% peak height.

6.2 Radio frequency generator compliant with FCC regulations.

6.3 Argon Gas Supply: High purity grade (99.99%)

6.4 Variable Speed Peristaltic Pump

6.5 Mass Flow Controller for the Nebulizer Gas Supply

6.6 Water Cooled Spray Chamber

6.7 Class A, Volumetric Flasks.

6.8 Volumetric pipettes: Calibrated daily at volumes bracketing the points of use.

6.9 Analytical balance with capability to measure 0.1 mg

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Due to the sensitivity of the ICP/MS, all reagents must be high-purity, whenever possible. All acids used for this procedure must be ultra high-purity grade suitable for trace metal analysis.

7.1.1 Nitric Acid, concentrated ($HNO_{3})$

7.1.1 Nitric Acid. 1:1 Solution (HNO_3 1:1)

7.1.6 Reagent/Nanopure Water

7.2 Standard Solutions

7.2.1 Certified, prepared stock standard solutions are purchased from commercial vendors, Spex and from Inorganic Ventures. Multi-element standards are prepared in the laboratory by diluting the stock-standard solutions in a 2% nitric acid solution. Example "recipes" for prepared intermediate and working standard solutions are given in Tables 2-11.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT & STORAGE

8.1 Samples should be collected in 50 or 1000 mL polyethylene containers. Aqueous samples for total metals analysis must be preserved with nitric acid to a pH less than 2 immediately following collection. Soil samples and aqueous samples for dissolved metals analysis should not be preserved in the field. Immediately following collection, samples must be cooled to 4°C (± 2°C) during shipment. Unpreserved samples should be maintained at that temperature until the time of digestion.

8.2 Aqueous samples for dissolved metals must be filtered and preserved prior to digestion. However, sample digestion must not begin until 16 hours after preservation has occurred.

8.3 The holding time for all samples is 180 days from time of collection. Samples and digestates are stored from the time of receipt in the laboratory until 60 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or client-specific protocol, samples and digestates are disposed of after 60 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

This section describes the quality control (QC) requirements uses to assess ongoing performance for each determinative method covered by this SOP. Except where noted, the laboratory adheres to the QC program and performance criteria for the determinative method being performed. For example, the CLP SOW requires analysis of a CRQL standard thus when CLP SOW is performed a CRQL standard is analyzed. A QC summary is provided in Table 12 along with the method criteria and recommended corrective action. The requirements for initial method performance are given in section 14.0.

9.1 Method Blank (MB)

For each analytical batch of 20 or fewer samples, a method blank (MB) is analyzed to assess potential contamination from the laboratory environment. The analyte values in the MB must be less than the reporting limit for all analytes of interest. When values in the MB exceed the reporting limit, contamination should be suspected. The source of contamination should be identified and corrected and samples should be re-prepared and reanalyzed for the affected analytes.

9.2 Laboratory Control Sample (LCS)

For each analytical batch of 20 or fewer samples, a laboratory control sample (LCS) is analyzed. The recovery of the LCS should be within the established accuracy limits for the determinative method performed. For samples analyzed by SW-846 Method 6020 and CLP SOW ILM04.1 and ILM05.2, the control limit is ± 20% of the true value. For samples analyzed by EPA Method 200.8, the control limit is ± 15% of the true value.

9.3 Instrument Performance Checks

Instrument performance is checked on a continuing basis using calibration blanks and calibrations standards following each calibration routine (ICV, ICB), after every ten analyses and at the end of the run (CCB, CCV). The results of the checks indicate if the calibration is still valid. If the calibration is not confirmed within the specified limit for the ICV, then the instrument must be recalibrated. If the continuing calibration checks are not confirmed, then the samples bracketed by the failing standard must be reanalyzed.

9.3.1 Initial Calibration Verification (ICV)

The ICV standard is obtained from a source independent than the calibration standards and is used to verify the accuracy of the initial calibration. The concentration of the ICV solution should be at or near the midpoint of the linear range of the calibration curve and should include every analyte for each mass used to report results. The percent recovery of the ICV standard must be ± 10% of the true value.

9.3.2 Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

A calibration blank is analyzed immediately following every ICV and CCV, and at the beginning and end of each analytical run. The concentration of the ICB/CCB must be less than the established reporting limit.

9.3.3 Continuing Calibration Verification (CCV)

The CCV standard is analyzed at a frequency of every ten samples. The analyte concentration of the CCV is different than the ICV and is typically at a concentration near the midpoint of the calibration curve. The percent recovery of the CCV must be ± 10% of the true value, except for samples analyzed by EPA Method 200.8, for which the percent recovery of the CCV must be ± 15% of the true value.

9.3.4 ICS Solutions (ICSA, ICSB)

The ICSA and ICSB solutions are analyzed after the ICB and after the CRI standard (when performed). The ICSA, ICSB are used to monitor instrument performance in the presence of known interferents. The recovery of each analyte in the ICSA/B solution should be ± 20% of the true value.

9.3.5 CRQL (CRI) Check Standard

To verify linearity near the CLP SOW contract required quantitation limit, a CRI standard is analyzed at the beginning (but not before the ICV) when CLP SOW analysis is performed. The percent recovery and frequency of the CRI standard should be within the established control limits specified in the CLP SOW.

9.4 Matrix Spike (MS) & Post Digestion Spike

Matrix spikes are analyzed at a frequency of one per 20 samples per site-specific matrix. The MS is used to provide information to the client about the effect of a site-specific matrix on the analytical procedure. A post digestion spike is performed for every sample that was used as a matrix spike to evaluate matrix interference and the percent recovery should be within 75-125% of the true value. For EPA Method 200.8, the percent recovery should be within 70-130% of the true value.

9.5 Serial Dilution

For each analytical batch of 20 or fewer samples, a serial dilution is performed and the concentration is compared with that of the parent sample. The results should agree within ± 10%. If not, then a interference effect may be suspected.

9.6 Internal Standard

Internal standards are used to check and correct for instrument drift and physical interference. A list of internal standards used is given in Table 2. The internal standards are added to all samples, standards, and QC samples in the same manner and at the same concentration. The recovery of the internal standard should be between 60 and 120% of the magnitude of the internal standard in the initial calibration.

10.0 CALIBRATION & STANDARDIZATION

10.1 Instrument Operating Conditions & Precalibration Routine

10.1.1 Initiate and set-up the operating parameters of the instrument following the instructions provided by the instrument manufacturer. The plasma, sample uptake parameters and the power levels are fixed and set to the recommended level for optimal sensitivity and to minimize interferents. Allow the instrument to equilibrate (warm-up) for at least 30 minutes prior to analysis. Check the sample flow through the pump tubing to ensure that flow to the nebulizer and drain flow is smooth. If the flow is erratic, check the tubing placement on the pump rollers and replace, as necessary.

10.1.2 Tune Standard

The tune standard solution contains a range of isotope masses used to establish the accuracy, resolution and precision of the ICP-MS prior to instrument calibration. The relative standard deviation of the integrations must be <5. The concentration of the tune standard solution is given in Table 3.

Analyze the tune standard solution five times consecutively. The percent standard deviation of the absolute signals for all analytes in the tune standard solution must be less than or equal to 5%. Use the template labeled “Daily Stability Check” to ensure this step is performed consistently each time. If the %RSD is greater than 5%, reanalyze the tune standard to ensure the instrument has reached thermal stability. If repeat failure, investigate the cause of the problem and correct prior to calibration.

10.1.3 Perform initial mass calibration and resolution checks in the mass regions of interest. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration shall be adjusted to the correct value. The resolution should also be verified to be less than 0.9 amu full width at 10 percent peak height.

10.2 Initial Calibration

10.2.1 Calibrate the instrument at the start of each analytical run with a blank and three standards. Fortify the calibration standard solutions with 1 ml of internal standard solution per 100 ml of calibration standard solution. Perform three replicate integrations and use the average of the three integrations for instrument calibration and quanitifcation. The correlation coefficient for the curve must be >0.995 for each analyte of interest in order to proceed with analysis.

10.3 System Performance Checks & Analytical Sequence

10.3.1 Following calibration, analyze the check standards and ensure that the performance is within the established criteria before proceeding with sample analysis. If criteria are not met, stop analysis, investigate and correct the problem. If necessary, recalibrate and start over. Each check standard must be fortified with the same proportion of internal standard solution as was added to the calibration standards. An example sequence is given below:

ICV
ICB
CRI (if applicable)
ICSA
ICSAB
CCV (repeat after every ten samples and at end of analytical sequence)
CCB (repeat after every ten samples and at end of analytical sequence)

A monitored rinse cycle (rinse blank) is used between each acquisition to remove traces of the previous sample. The minimum rinse time is set to 120 seconds. Detector-mass calibration and cross calibration are re-determined as needed or whenever a major change (i.e. installation of new detector) in instrumentation is implemented.

11.0 PROCEDURE

11.1 Digest samples following approved laboratory standard operating procedures for sample preparation.

11.2 Prepare the digestates/sample for analysis by transferring 9.9 ml aliquot into an autosampler tube to which 0.1 mL of internal standard solution was added.

11.3 On the PC connected to the instrument, select the template labeled "6020". Enter the sample ID's in the space provided in the order the samples were placed in the austosampler. Delete any extra spaces, select the most current instrument configuration tab, and then select the "Q" icon to begin the analytical run.

11.4 After data acquisition, review the sample results and evaluate the internal standard recovery. If criteria are not met for any sample, dilute and reanalyze. Samples with target concentrations that exceed the linear range must be diluted and reanalzyed.

11.5 Quantitative results should be reported in appropriate units and significant figures and must be corrected for dilutions and percent solids. The calculations performed by the data acquisition system include interference correction and internal standard normalization. The equations used to generate concentrations by the data handling system are given in section 12.0.

11.6 Unless otherwise specified by client or regulatory program, sample results are reported to the IDL. Results between the IDL and RL are qualified as estimated values with a "B" data flag.

12.0 CALCULATIONS

12.1 Equation 1: Sample Concentration / Aqueous Sample

$C_{(\mu g/L)} = \mu g/L_{DIG} * (V_{DIG}/V_{SAMP})$

Where:
μ/L_{DIG} = ICP-MS Result
V_{DIG} = Digestate volume in mL
V_{SAMP} = Sample volume in mL

12.2 Equation 2: Sample Concentration / Soil, Sediment Sample

$C_{(mg/kg)} = \mu g/L_{DIG} * (V_{DIG}/G_{SAMP})$

Where:
μ/L_{DIG} = ICP-MS Result
V_{DIG} = Digestate volume in liters
G_{SAMP} = Sample weight in grams

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Review the samples, standards and QC samples against the performance criteria given in section 9.0 for Quality Control. If the results do not fall within the established limits or criteria, corrective action is required. A QC Summary is provided in Table 2 along with recommended corrective actions for each test method. If corrective action is not taken or unsuccessful, the situation should be documented and reported in the project narrative. All data that does not meet established criteria must be flagged with the appropriate data qualifier and noted in the project narrative.

14.0 METHOD PERFORMANCE

14.1 An Initial Demonstration of Capability is required for each analyst before unsupervised performance of this method.

14.2 An Initial Method Detection Limit (MDL) determination for each test method referenced in this SOP is performed following the procedure described in the reference method, 40CFR, Part 136, Appendix B and laboratory SOP LP-LB-009. The MDL is verified or repeated when a significant change to the method occurs. Significant changes include the use of alternate reagents or standard reference materials, new instrumentation or the use of alternate sample preparation procedures.

14.3 Instrument Detection Limits (IDL) are determined quarterly by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a low-level standard solution.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 The laboratory optimizes technology to minimize pollution and reduce the production of hazardous waste whenever possible.

15.2 The laboratory procedures for waste management comply with applicable federal, state and local regulations and are described in SOP LP-LB-001HAZWD.

16.0 REFERENCES

16.1 *Determination of Trace Elements in Waters and Waters by Inductively Coupled Plasma-Mass Spectrometry (Method 6020),* Revision 0; September 1994. USEPA SW-846 Methods for Evaluating Solid Waste, Update III.

16.2 *Multi-Media, Mulit-Concentration SOW for Inorganic Analyes, ILM05.2,* December 2001, USEPA Contract Laboratory Program.

16.3 *EPA Method 200.8, Revision 5.4, 1994.* US EPA Office of Research and Development, Cincinnati, Ohio

17.0 TABLES, DIAGRAMS, FLOWCHARTS

17.1 Table 1: *Analyte List and Reporting Limits*
17.2 Table 2: *Recommended Internal Standard Component and Concentrations*
17.3 Table 3: *Recommended Tune Standard Component and Concentrations*
17.4 Table 4: *Recommended Intermediate Calibration Standard Components and Concentrations*
17.5 Table 5: *Recommended Working Calibration Standard Components and Concentrations*
17.6 Table 6: *Recommended Intermediate Standard Components and Concentrations for the ICV*
17.7 Table 7: *Recommended Working Standard Components and Concentrations for the ICV and LCS*
17.8 Table 8: *Recommended ICSA Working Standard Components and Concentrations (6020ICS-0A)*
17.9 Table 9: *Recommended ICSB Working Standard Components and Concentrations (6020ICS-0B)*
17.10 Table 10: *Recommended ICSAB Intermediate Standard Components and Concentrations*
17.11 Table 11: *Recommended ICSAB Working Standard Components and Concentrations*
17.12 Table 12: *QC Summary & Recommended Corrective Action*

Table 1: Target List and Reporting Limit (ICP-MS)

Element		CAS Number	Isotope (amu)	Reporting Limit		
				(All Methods) Aqueous ug/L	(SW846) Soil/Sediment mg/Kg	(CLP) Soil/Sediment mg/Kg
Al	Aluminum	7429-90-5	27	40	4	8
Sb	Antimony	7440-36-0	123	20	2	4
As	Arsenic	7440-38-2	75	2.0	0.2	0.4
Ba	Barium	7440-39-3	135	100	10	20
Be	Beryllium	7440-41-7	9	2	0.2	0.4
B	Boron	7440-42-8	11	20	2	4
Cd	Cadmium	7440-43-9	111	2	0.2	0.4
Ca	Calcium	7440-70-2	44	1000	100	200
Cr	Chromium	7440-47-3	52	4.0	0.4	0.8
Co	Cobalt	7440-48-4	59	10	1	2
Cu	Copper	7440-50-8	65	20	2	4
Fe	Iron	7439-89-6	54	200	20	40
Pb	Lead	7439-92-1	208	2.0	0.2	0.4
Mg	Magnesium	7439-96-5	25	1000	100	200
Mn	Manganese	7439-96-5	55	4.0	0.4	0.8
Mo	Molybdenum	7439-98-7	98	20	2	4
Ni	Nickel	7440-02-0	60	20	2	4
K	Potassium	7440-09-7	39	1000	100	200
Se	Selenium	7782-49-2	82	2.0	0.2	0.4
Ag	Silver	7440-22-4	107	2.0	0.2	0.4
Na	Sodium	7440-23-5	23	1000	100	200
Tl	Thallium	7440-28-0	205	2.0	0.2	0.4
V	Vanadium	7440-62-2	51	4.0	0.4	0.8
Zn	Zinc	7440-66-6	66	20	2	4

Table 2: Recommended Component and Concentration for the Internal Standard Solution

Element	Concentration (ug/L)	Mass (amu)
Li	1300	6 and 7
Y	5	89
Sc	10	45
Tb	2.5	159
Bi	5.5	209
In	5	115

Table 3: Recommended Tune Standard Components and Concentrations

Element	**Stock Standard Concentration (mg/L)**	**Volume (mL)**	**Final Volume (mL)**	**Final Concentration (ug/L)**
Li	10000	0.02	200	10
Be	1000	0.2	200	10
Mg	10000	0.02	200	10
Al	10000	0.02	200	10
Sc	1000	0.2	200	10
V	1000	0.2	200	10
Co	1000	0.2	200	10
Y	10000	0.02	200	10
In	1000	0.2	200	10
Ba	1000	0.2	200	10
Ce	1000	0.2	200	10
Tb	1000	0.2	200	10
Pb	1000	0.2	200	10
Th	1000	0.2	200	10
U	1000	0.2	200	10
Bi	1000	0.2	200	10

*Prepare by mixing the specified volume of individual element stock standard solutions into 200 mL 2 % nitric acid solution to produce a concentration of 10 ug/L of each element.

* The above table includes a "recipe" for the preparation of a working standard solution using commercially individual element stock standard solutions at a recommended concentration. Should the concentrations of the stock standards differ from those listed in the table, the preparation steps and concentrations must be adjusted accordingly.

Table 4: Recommended Intermediate Calibration Standard Components and Concentrations

Element	Stock Standard Concentration mg/L	Initial Volume mL	Final Volume mL	Final Concentration mg/L
Al	10,000	2.0	500	40
Sb	1000	10	500	20
As	1000	1.0	500	2.0
Ba	1000	50	500	100
Be	1000	1.0	500	2.0
B	1000	10	500	20
Cd	1000	1.0	500	2.0
Ca	10,000	50	500	1000
Cr	1000	2.0	500	4.0
Co	1000	5.0	500	10
Cu	1000	10	500	20
Fe	10,000	10	500	200
Pb	1000	1.0	500	2.0
Mg	10,000	50	500	1000
Mn	1000	2.0	500	4.0
Mo	1000	10	500	20
Ni	1000	10	500	20
K	10,000	50	500	1000
Se	1000	1.0	500	2.0
Ag	1000	1.0	500	2.0
Na	10,000	50	500	1000
Tl	1000	1.0	500	2.0
V	1000	2.0	500	4.0
Zn	1000	10	500	20

*Prepare by mixing the specified volume of individual element stock standard solutions into 500 mL 2 % nitric acid solution to produce the specified concentration of each element.

* The above table includes a "recipe" for the preparation of an intermediate standard solution using individual element stock standard solution at a recommended concentration. Should the concentrations of the stock standards differ from those listed in the table, the preparation steps and concentrations must be adjusted accordingly.

Table 5: Recommended Working Calibration Standard Components and Concentrations

* KLM 11/18/02

Element	Intermediate Calibration Standard (mg/L)	Calibration Level 3			Calibration Level 2 (made from Cal 3)			Calibration Level 1 (made from Cal 3)		
		Initial Volume mL	Final Volume mL	Final Concentration μ~~m~~g/L	Initial Volume mL	Final Volume mL	Final Concentration μ~~m~~g/L	Initial Volume mL	Final Volume mL	Final Concentration μ~~m~~g/L
Al	40	25	1000	1000	100	500	200	20	500	40
Sb	20	25	1000	500	100	500	100	20	500	20
As	2.0	25	1000	50	100	500	10	20	500	2.0
Ba	100	25	1000	2500	100	500	500	20	500	100
Be	2.0	25	1000	50	100	500	10	20	500	2.0
B	20	25	1000	500	100	500	100	20	500	20
Cd	2.0	25	1000	50	100	500	10	20	500	2.0
Ca	1000	25	1000	25000	100	500	5000	20	500	1000
Cr	4.0	25	1000	100	100	500	20	20	500	4.0
Co	10	25	1000	250	100	500	50	20	500	10
Cu	20	25	1000	500	100	500	100	20	500	20
Fe	200	25	1000	5000	100	500	1000	20	500	200
Pb	2.0	25	1000	50	100	500	10	20	500	2.0
Mg	1000	25	1000	25000	100	500	5000	20	500	1000
Mn	4.0	25	1000	100	100	500	20	20	500	4.0
Mo	20	25	1000	500	100	500	100	20	500	20
Ni	20	25	1000	500	100	500	100	20	500	20
K	1000	25	1000	25000	100	500	5000	20	500	1000
Se	2.0	25	1000	50	100	500	10	20	500	2.0
Ag	2.0	25	1000	50	100	500	10	20	500	2.0
Na	1000	25	1000	25000	100	500	5000	20	500	1000
Tl	2.0	25	1000	50	100	500	10	20	500	2.0
V	4.0	25	1000	100	100	500	20	20	500	4.0
Zn	20	25	1000	500	100	500	100	20	500	20

Note: The above table includes a "recipe" for the preparation of the working calibration standards using a multi-element intermediate standard prepared in the laboratory at a recommended concentration. Should the concentrations of the intermediate standard differ from those listed in the table, the preparation steps and concentrations for the working standards must be adjusted accordingly.

Table 6: Recommended Intermediate Standard Components and Concentrations for the ICV

Element	Stock Standard Concentration mg/L	Initial Volume mL	Final Volume mL	Final Concentration mg/L
Al	10,000	1.0	200	50
Sb	1000	5.0	200	25
As	1000	0.5	200	2.5
Ba	1000	25	200	125
Be	1000	0.5	200	2.5
B	1000	5.0	200	2.5
Cd	1000	0.5	200	2.5
Ca	10,000	25	200	1250
Cr	1000	1.0	200	5.0
Co	1000	2.5	200	12.5
Cu	1000	5.0	200	25
Fe	10,000	5.0	200	250
Pb	1000	0.5	200	2.5
Mg	10,000	25	200	1250
Mn	1000	1.0	200	5.0
Mo	1000	5.0	200	25
Ni	1000	5.0	200	25
K	10,000	25	200	1250
Se	1000	0.5	200	2.5
Ag	1000	0.5	200	2.5
Na	10,000	25	200	1250
Tl	1000	0.5	200	2.5
V	1000	1.0	200	5.0
Zn	1000	5.0	200	25

*Prepare by mixing the specified volume of individual element stock standard solutions into 200 mL 2 % nitric acid solution to produce a concentration of 10 ug/L of each element.

*The above table includes a "recipe" for the preparation of an intermediate standard solution using individual elements at a recommended concentration. Should the concentrations of the individual stock standards differ from those listed in the table, the preparation steps and concentrations of the intermediate standard must be adjusted accordingly.

Table 7: Recommended Working Standard Components and Concentrations for the ICV and LCS

Element	ICV Intermediate Standard Concentration mg/L	Initial Volume mL	Final Volume mL	Final Concentration ug/L
Al	50	5	500	500
Sb	25	5	500	250
As	2.5	5	500	25
Ba	125	5	500	1250
Be	2.5	5	500	25
B	2.5	5	500	250
Cd	2.5	5	500	25
Ca	1250	5	500	1250
Cr	5.0	5	500	50
Co	12.5	5	500	125
Cu	25	5	500	250
Fe	250	5	500	2500
Pb	2.5	5	500	25
Mg	1250	5	500	1250
Mn	5.0	5	500	50
Mo	25	5	500	250
Ni	25	5	500	250
K	1250	5	500	12500
Se	2.5	5	500	25
Ag	2.5	5	500	25
Na	1250	5	500	12500
Tl	2.5	5	500	25
V	5.0	5	500	50
Zn	25	5	500	250

*Prepare by mixing the specified volume of intermediate standard solution into 500 mL 2 % nitric acid solution to produce the desired concentration of each element.

*The above table includes a "recipe" for the preparation of working standard solutions using an intermediate standard solution prepared in the laboratory at a recommended concentration. Should the concentrations of the intermediate standard differ from those listed in the table, the preparation steps and concentrations for the working standards must be adjusted accordingly.

Table 8: Recommended ICSA Working Standard Components and Concentrations (6020ICS-0A)

Element	Stock Standard Concentration mg/L	Initial Volume mL	Final Volume mL	Final Concentration mg/L
Cl	10,000	20	200	1000
Ca	1000			100
Fe	1000			100
Na	1000			100
C	2000			200
Al	1000			100
Mg	1000			100
P	1000			100
K	1000			100
S	1000			100
Mo	20			2.0
Ti	20			2.0

*Prepare by mixing 20 mL of the stock standard solution into 200 mL 2% nitric acid solution.

*The above table includes a "recipe" for the preparation of a working standard solution using a multi-element stock standard solution at a recommended concentration. Should the concentration of the stock standard differ from those listed in the table, the preparation steps and concentrations for the working standard must be adjusted accordingly.

Table 9: Recommended ICSB Working Standard Components and Concentrations (6020ICS-0B)

Stock Standard*	Concentration mg/L
As	2.0
Cd	2.0
Cr	2.0
Co	2.0
Cu	2.0
Mn	2.0
Ni	2.0
Ag	2.0
Zn	2.0

* Multi-element stock standard purchased from Inorganic Venture.

Table 10: Recommended ICSAB Intermediate Standard Components and Concentrations

Element	Stock Standard Concentration mg/L	Initial Volume mL	Final Volume mL	Final Concentration mg/L
Sb	1000	5.0	100	50
Ba	1000	25	100	250
Be	1000	1.0	100	10
B	1000	5.0	100	50
Cr	1000	1.0	100	10
Co	1000	1.5	100	15
Cu	1000	4.0	100	40
Pb	1000	1.0	100	10
Mn	1000	1.0	100	10
Ni	1000	4.0	100	40
Se	1000	1.0	100	10
Tl	1000	1.0	100	10
V	1000	2.0	100	20
Zn	1000	4.0	100	40

*Prepare by mixing individual element stock standard solutions into 100 mL 2% nitric acid solution.

*The above table includes a "recipe" for the preparation of an intermediate standard solution using individual element stock standard solutions at a recommended concentration. Should the concentrations of the stock standards differ from those listed in the table, the preparation steps and concentrations for the working standards must be adjusted accordingly.

Table 11: Recommended ICSAB Working Standard Components and Concentrations

Intermediate Standard	**Final Concentration ug/L**
Al	100,000
Sb	100
As	20
Ba	500
Be	20
B	100
Cd	20
Ca	100,000
Cr	40
Co	50
Cu	100
Fe	100,000
Pb	20
Mg	100,000
Mn	40
Mo	2000
Ni	100
K	100,000
Se	20
Ag	20
Na	100,000
Tl	20
V	40
Zn	100

*Prepare by mixing 50 mL of 6020ICS-0A Working Standard Solution, 5.0 mL of 6020ICS-0B Working Standard Solution, and 1.0 mL of ICSAB Intermediate Standard Solution in a volumetric flask that contains 500 mL of Nanopure Water and 2% nitric acid.

*The above table includes a "recipe" for the preparation of a working standard solution using an intermediate standard solutions prepared in the laboratory at a recommended concentration. Should the concentrations of the intermediate standards differ from those listed in the table, the preparation steps and concentrations for the working standards must be adjusted accordingly.

Table 12: QC Summary & Recommended Corrective Action

QC Item	Frequency	Acceptance	Recommended Corrective Action*
ICP-MS Tune Standard	24 Hours	% RSD <5	System Check, Reanalyze
ICAL Blank + 3 Standards	As Required	Correlation Coefficient <0.995	System Check, Reanalyze
ICV	Following ICAL	%R ± 10% of true value	System Check, Reanalyze, Prepare new standard solutions, Recalibrate, Reanalyze
CCV	After ICSAB and after every 10 analytical samples	%R ± 10% of true value	System Check, Recalibrate. Reanalyze any samples not bracketed by acceptable CCV.
ICB/CCB	Following each ICV/CCV	Target < RL	System Check, Recalibrate
ICSA & ICSAB Solution	After each ICB and/or CRI	%R ± 20% of true value	System Check, Recalibrate
CRI Check Standard (CLP)	After ICB	%R within limits specified in SOW	System Check, Recalibrate
Method Blank	With each sample batch of 20 samples or less	Target < RL	Reanalyze with associated samples
Lab Control Sample	With each sample batch of 20 samples or less	Aqueous: %R ± 20% of true value Soil: %R within vendor limits	System Check, Reanalyze, Recalibrate, Reprep
Internal Standards	Every blank, sample, standard	%R 60-120% of magnitude of internal standard in ICAL	Dilute samples as needed. Reanalyze. If repeat failure, qualify result.
Matrix Spike	With every 20 field samples or as needed	%R (75-125)	Evaluate sample concentration. If the sample concentration exceeds the concentration of spike added by a factor of four or more, report data. Otherwise, qualify with "N" and perform post digestion spike.
Post Digestion Spike	Each MS	NA	
Sample Duplicate	With every 20 field samples or as needed	%RPD ± 20% of original sample determination	Flag result with "*"
Serial Dilution	One sample from each batch	%D ± 10% of original sample determination	Evaluate internal standard recovery. If internal standards OK, suspect interference and qualify data with "E".

**The recommended corrective action may include some or all of the items listed in this column. The analyst must use professional judgement to investigate and correct problems before proceeding with analysis. Suspect data must be qualified and reported in the project narrative.*

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APPENDIX A-89

METHOD EPH_MA: AN STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS – MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION

METHOD: EPH_MA:AN
STANDARD OPERATING PROCEDURE
FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS – MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION

Applicable matrix or matrices: Soils, Waters
Standard Compound List and Reporting Limits: See Section 19.0

Approvals and Signatures

Laboratory Director: Christopher A. Ouellette Date: 8/8/0

QA Manager: Kim B. Watson Kim B. Watson Date: 8/8/00

GC Laboratory Manager David Downing Dave Downing Date: 8/8/00

Organic Technical Director: Bryce E. Stearns Date: 8/8/00

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of extractable aliphatic and aromatic hydrocarbons in water and soil extracts. The aliphatic hydrocarbons are quantitated as C_9 through C_{18} and C_{19} through C_{36} ranges. The aromatic hydrocarbons are quantitated in the C_{11} through C_{22} range. Individual polynuclear aromatic hydrocarbons (PAH) are also quantitated using this method.

1.2 Like all GC procedures, this method is subject to a "false positive" bias in the reporting of Target PAH Analytes, in that non-target hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantified as a Target or Diesel PAH Analyte. While cleanup procedures specified in this method to segregate aliphatic and aromatic fractions will serve to mitigate this concern, confirmatory analysis by dissimilar columns, gas chromatography/mass spectrometry (GC/MS) analysis, or other suitable technique is recommended in cases where a target PAH analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where coelution of a non-target hydrocarbon compound is suspected.

2.0 SUMMARY OF METHOD

2.1 This method provides the sample preparation and gas chromatographic conditions that will be applied to analyze extractable aliphatic and aromatic hydrocarbons based on the method prepared by the Massachusetts Department of Environmental Protection. Detection limits are presented in Section 19.0

2.2 Prior to sample analysis, the gas chromatograph equipped with a flame ionization detector (FID) is calibrated using five point calibration curves. Calibration curves using an aliphatic hydrocarbon standard mixture are used to calculate the C_9 through C_{18} and C_{19} through C_{36} aliphatic hydrocarbons. A calibration curve using a PAH standard mixture is used to calculate the C_{11} through C_{22} aromatic hydrocarbon concentration. Instrument stability is verified every ten sample injections with the mid point standard.

3.0 DEFINITIONS

3.1 Laboratory Reagent Blank (LRB) or Method Blank (XBLK##) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB or XBLK## is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.2 Instrument Performance Check Solution (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.3 Laboratory Fortified Blank (LFB) or Laboratory Control Sample (LCS) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB or LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.4 Laboratory Fortified Matrix (LFM) or Matrix Spike and Matrix Spike Duplicate (MS/MSD) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM or MS/MSD is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM or MS/MSD corrected for background concentrations.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be free from interferences, under the conditions of the analysis.

4.2 Interferences coextracted from samples will vary considerably from source to source, depending upon the matrix being sampled.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 STL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in these methods. Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. STL also has a written environmental health and safety plan.

5.3 Please note chemicals that have the potential to be highly toxic or hazardous, the appropriate MSDS must be reviewed by the employee before handling the chemical.

6.0 EQUIPMENT AND SUPPLIES

6.1 Gas Chromatograph: An analytical system equipped with a packed or split/splitless injection port, flame ionization detector, and an auto-sampler.

6.2 Data System: The data system must be capable of handling a minimum of 200 chromatographic peaks per detector. Fison's VAX based multi-chrom version 2.0 is used for this analysis.

6.3 Fused Silica Capillary Column

6.3.1 DB-5ms, (5%-phenyl)-methylpolysiloxane

6.3.2 DB-35ms, (35%-phenyl)-methylpolysiloxane

6.4 GC Set-Up

6.4.1 GC Configuration: A five meter deactivated guard column is installed into the injection port. The guard column is connected using a "y" connector to the two analytical columns, which are each installed into a flame ionization detector.

6.4.2 Operating Conditions: Operating conditions are used as guidelines to starting an analytical method. Conditions may change depending on the types of columns used (including different manufacturers). Both aromatic and aliphatic hydrocarbons are analyzed using these conditions.

Initial Temperature: 70°C
Time 1: 1.0 minute
Rate 1: 20°/min
Temperature 1: 250°C
Rate 2: 5°/min
Temperature 2: 320°C
Time 2: 5 min

7.0 REAGENTS AND STANDARDS

7.1 Solvents

7.1.1 Hexane - JT Baker, Resi-Analyzed, Cat #JT9262-3

7.1.2 Acetone - JT Baker, Resi-Analyzed, Cat #JT9254-3

7.1.3 Methylene Chloride - JT Baker, Ultra Resi-Analyzed, Certified Acid Free, Cat #JT9266-95

7.2 Standards

7.2.1 Aromatic Hydrocarbon Standard: This standard consists of 17 PAH compounds, fractionation surrogate, and a surrogate compound. It is used to define the retention times and responses for each PAH and establish the window for the C_{11} through C_{22} aromatic hydrocarbon concentration.

Table 1: Five Point Calibration Concentration (mg/L)

Compound	**STD1 (ppm)**	**STD2 (ppm)**	**STD3 (ppm)**	**STD4 (ppm)**	**STD5 (ppm)**
naphthalene	5	10	20	40	80
2-methylnaphthalene	5	10	20	40	80
2-fluorobiphenyl (fractionation surrogate)	5	10	20	40	80
acenaphthylene	5	10	20	40	80
acenaphthene	5	10	20	40	80
fluorene	5	10	20	40	80
phenanthrene	5	10	20	40	80
anthracene	5	10	20	40	80
o-terphenyl (surrogate)	5	10	20	40	80
fluoranthene	5	10	20	40	80
pyrene	5	10	20	40	80
benzo(a)anthracene	5	10	20	40	80

Compound	STD1 (ppm)	STD2 (ppm)	STD3 (ppm)	STD4 (ppm)	STD5 (ppm)
chrysene	5	10	20	40	80
Benzo(b)fluoranthene	5	10	20	40	80
benzo(k)fluoranthene	5	10	20	40	80
benzo(a)pyrene	5	10	20	40	80
indeno(123-cd)pyrene	5	10	20	40	80
dibenz(ah)anthracene	5	10	20	40	80
benzo(ghi)perylene	5	10	20	40	80

7.2.2 Aliphatic Hydrocarbon Standard: This standard is a 14 component mixture of normal alkanes and a surrogate compound. This standard defines the windows for the two aliphatic hydrocarbon ranges and is used to calculate the collective concentration of aliphatic hydrocarbons within those ranges.

Table 2: Aliphatic Hydrocarbon Standard Concentrations

Compound	Carbon Number	STD1 (ppm)	STD2 (ppm)	STD3 (ppm)	STD4 (ppm)	STD5 (ppm)
Nonane	9	5	10	20	40	80
Decane	10	5	10	20	40	80
Dodecane	12	5	10	20	40	80
Tetradecane	14	5	10	20	40	80
Hexadecane	16	5	10	20	40	80
Octadecane	18	5	10	20	40	80
Nonadecane	19	5	10	20	40	80
Eicosane	20	5	10	20	40	80
1-Chloro-octadecane (surrogate)		5	10	20	40	80
Docosane	22	5	10	20	40	80

Compound	**Carbon Number**	**STD1 (ppm)**	**STD2 (ppm)**	**STD3 (ppm)**	**STD4 (ppm)**	**STD5 (ppm)**
Tetraosane	24	5	10	20	40	80
Hexacosane	26	5	10	20	40	80
Octacosane	28	5	10	20	40	80
Triacontane	30	5	10	20	40	80
Hexatriacontane	36	5	10	20	40	80

7.2.3 Fractionation Check Standard: This standard is prepared in hexane containing 25 mg/L of the above 14 alkanes and 17 PAHs. It is eluted through the silica gel to monitor the fractionation efficiency of the silica gel. This is performed each time a new manufacturer's lot of silica gel is used.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Aqueous samples must be extracted within 14 days of collection and analyzed within 40 days of extraction. Aqueous samples must be preserved to a pH < 2. KBW 12/1/00 1:1 HCl

8.2 Soil and sediment samples must be extracted within 7 days of collection and analyzed within 40 days of extraction.

8.3 Sample extracts are preserved in a refrigerator at 4 ± 2°C.

9.0 QUALITY CONTROL

9.1 Method Blank: One per extraction batch, Sample Delivery Group (SDG), or every 20 samples. All analytes must be less than the quantitation limit. If a method blank fails, all samples in the associated extraction group must be re-extracted.

9.2 Surrogate Standard Compounds: Method blank and samples are fortified with surrogate spike before extraction begins. Surrogate compounds and recovery limits are listed below in Table 3.

Table 3: Recovery Limits for Surrogate Compounds

Compound	Water (%R)	Soil (%R)
o-terphenyl (aromatic surrogate)	40-140	40-140
1-chloro-octadecane (aliphatic surrogate)	40-140	40-140
2-fluorobiphenyl (fractionation surrogate)*	40-140	40-140

*Fractionation surrogate elutes with aromatic fraction.

Individual component recoveries are calculated with the following equation:

$$\textit{Surrogate Recovery (\%)} = \frac{SR}{SA} * 100$$

Where:
SR = Spike Result
SA = Spike Added (concentration)

Although recovery limits are advisory, if recovery of any surrogate compound is outside of these limits, then the sample analysis is thoroughly reviewed and the sample extract may be reanalyzed and possibly re-extracted if the surrogate recovery confirms low. The client will be notified of any gross deficiencies in surrogate recovery to discuss possible corrective action.

9.3 MS/MSD and LCS: An MS/MSD analysis is required every 20 samples. The MS/MSD analysis consists of fortifying two aliquots of the same sample with matrix spike solution before extraction begins. The Laboratory Control Sample (LCS) is required with every extraction batch. The spike recovery for each of these QC samples must be within 40-140% of the true value. The relative percent difference between the MS/MSD samples must not exceed 50%.

If recovery of any matrix compound is outside of these limits, then the sample analysis is thoroughly reviewed and the sample extract may be reanalyzed or possibly re-extracted depending on circumstances. The client will be notified of any gross deficiencies in matrix recovery to discuss possible corrective action.

Matrix spike results will be reviewed in conjunction with surrogate recoveries to evaluate method performance.

Individual component recoveries are calculated with the following equation:

$$MS\ Recovery\ (\%) = ((SSR-SR)/SA))*100$$

Where:
SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

The Relative Percent Difference (%RPD) between matrix spike and matrix spike

$$\%\ RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

duplicate analysis is calculated with the following equation:

Where:
RPD = Relative Percent Difference
D_1 = First Sample Value
D_2 = Second Sample Value (duplicate)

Table 4: Quality Control and Corrective Action

Extractable Petroleum Hydrocarbons _ MA			
Quality Control Criteria	**Frequency**	**Acceptance**	**Corrective Action**
Initial calibration	As Required	Correlation coefficient ≥ 0.995, linear regression.	Recalibrate, mix new standards, reanalyze
Initial Calibration Verification (ICV)	For each ICAL	± 25% for the quantitation column	Re-shoot, check integrations, mix new std.
Continuing Calibration Verification (CCV)	Every 10 samples	± 25% for the quantitation column	Re-shoot, check integrations, mix new std. Reanalyze ICAL

Extractable Petroleum Hydrocarbons _ MA			
Quality Control Criteria	**Frequency**	**Acceptance**	**Corrective Action**
Method Blank (XBLK##)	Each extraction batch	Targets < Reporting	Reanalyze, check for contamination, correct as required

Samples	--	Concentrations below highest calibration standard	Dilute and reanalyze samples that are more concentrated than the highest calibration standard
Surrogates and Fractionation Surrogate Spike	Every sample, blank and QC sample must be spiked with surrogate	40-140% Recovery	Any sample with outages must be reanalyzed to confirm. Present both sets of data.
Matrix Spike/Matrix Spike Duplicate	1 set every 20 samples, full compound list spike required	40-140% Recovery	Evaluate LCS. If compounds failing in MS/MSD are acceptable in the LCS the outages will assume to be matrix related.
LCS	Each extraction batch (full compound list; independent std)	40-140% Recovery 50% RPD	Check std., check quantitation, evaluate MS/MSD. Reanalyze batch if failing compounds are present in the samples.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Initial Calibration:

10.1.1 Prior to sample analysis, a five point calibration for each compound is analyzed. The aromatic hydrocarbons and aliphatic hydrocarbons are analyzed separately. A typical calibration is as follows in Table 5.

Table 5: Calibration Run

Lab ID	Injection
EPH Std 1	1
EPH Std 2	2
EPH Std 3	3
EPH Std 4	4
EPH Std 5	5
PIBLK	6
Samples	7-16
PIBLK	17
EPH Std 3	18

10.1.2 The initial calibration must meet the following controls:

- For quantitation, the correlation coefficient (r) must be ≥0.995 using a linear regression or $r^2 \geq 0.990$.

- A collective calibration curve is established for each hydrocarbon range. To calculate the ranges the summation of the peak areas is plotted against the total mass injected. Below in Table 6 is a listing of the collective concentrations within each hydrocarbon range.

Table 6: Collective Concentrations in Each Hydrocarbon Range

Component	**Concentration (ppm)**				
	Std. 1	**Std. 2**	**Std. 3**	**Std. 4**	**Std. 5**
C_9 - C_{18}	30	60	120	240	480
C_{19} - C_{36}	40	80	160	320	640
C_{11} - C_{22}	85	170	340	680	1360

- The EPH ranges are defined by the following compound retention times in Table 7.

Table 7: Compound Retention Times

Range	**Beginning Marker**	**Ending Marker**
C_9 - C_{18} aliphatic	Nonane	just before Nonadecane
C_{19} - C_{36} aliphatic	Nonadecane	Hexatriacontane
C_{11} - C_{22} aromatic	Naphthalene	Benzo (g,h,i) Perylene

10.3 Continuing Calibration - Mid Point Calibration Check

As indicated in the analytical sequence in Table 5, a mid-point standard is used for checking instrument stability.

10.3.1 The mid-point calibration check (EPH Std 3) standard must be analyzed every 10 sample injections. In order to continue the analysis, the check standards must meet the following criteria:

- Each analyte's concentration must be ± 25% of the nominal concentration.

*%D = [(conc. (nominal) – conc. (calculated))/conc. (nominal)]*100*

- Retention times (of chromatographic peaks used for quantitation and confirmation analysis) must fall within the established windows.

- 0.25 and 0.32 mm ID columns must be within ± 0.04 minutes of the initial calibration.

10.3.2 If these quality control criteria are not met, standards may be reinjected a second time. If they still fail, GC maintenance must be performed to correct the problem and re-calibration is required.

10.4 If the GC has been left idle for more than 8 hours, the following standard must be acquired and pass QC limits before sample analysis begins.

- EPH Std 3

10.5 When the sample analysis is completed, the analytical sequence must end with the EPH Std 3 standard.

11.0 PROCEDURE

Samples are prepared following extraction procedures of the MA DEP methodology. This method is based on a solvent extraction and fractionation by a silica gel column. In general, 1 liter of a water sample is extracted and concentrated to 1.0 mL. For soil/sediment samples, 10 grams is extracted and concentrated to 1.0 mL. Aliphatic and aromatic hydrocarbons are separated by elution through silica gel using solvents with different polarities. The final extract solvent is hexane.

12.0 CALCULATIONS

12.1 Compound concentrations will not be reported below the reporting limits stated in Table 8 in Section 19.0.

12.2 Quantitation

Water

*Sample conc. (mg/L) = extract conc. (mg/L) * [ext. vol. (L)/spl. Vol. (L)] * DF*

Soil

*Sample conc. (mg/Kg) = extract conc. (mg/L) * [ext. vol. (L)/spl. Wt. (Kg)]* ***(100/%solid)*****DF*

DF = Dilution Factor

12.3 Standard Qualifiers

U = Compound not detected at or above reporting limit.

E = Compound concentration exceeds the calibration range.

D = Compound concentration is reported from a secondary dilution of the sample.

13.0 METHOD PERFORMANCE

Method detection limits were calculated using the following formula:

$$MDL = S\ t_{(n-1,\ 1\text{-alpha} = 0.99)}$$

Where:
n = number of replicates
S = the standard deviation of the replicate analyses
$t_{(n-1,\ 1\text{-alpha} = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.0 DATA ASSESSMENT AND CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Technical acceptance criteria for sample analysis.

15.1.1 The samples must be analyzed on a GC system meeting the initial calibration, continuing calibration and blank technical acceptance criteria.

15.1.2 The sample must be analyzed within the required holding time.

15.1.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

15.1.4 The percent recovery of each of the system monitoring compounds in the sample must be within the acceptance windows.

15.1.5 The retention time shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the sample and the most recent continuing calibration standard analysis.

15.1.6 After analyzing a sample that exceeds the initial calibration range the analyst must either analyze an instrument blank (using the same purge inlet if using an auto sampler) which must meet technical acceptance criteria for blank analysis or monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the calibration range. The maximum contamination criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds that exceeded the limits in the contaminated sample. If auto sampler is used, the next sample analyzed using the same purge inlet must also meet the maximum contamination criteria. If the maximum criteria is exceeded, then all samples affected by the carryover must be re-analyzed.

15.2 Corrective Action for Sample Analysis.

15.2.1 Samples must meet technical acceptance criteria before reporting data.

15.2.2 Corrective action for failure to meet instrument performance checks, initial, continuing calibration, and method blanks must be completed prior to sample analysis.

15.2.3 Corrective action for system monitoring compounds that fail to meet acceptance criteria must be completed prior to sample analysis.

15.3 If any of the system monitoring compounds fail to meet acceptance criteria.

- ➢ Check all calculations, instrument logs, the system monitoring and the instrument operation. If the calculations were incorrect, correct calculations and verify that the system monitoring compound recovery responses meet acceptance criteria.

- ➢ Check the preparation of system monitoring compounds for concentration and expiration.

- ➢ Verify that the instrument is operating correctly.

15.4Determine if the problem was a matrix effect.

15.4.1 Check the surrogate recoveries for the MS and MSD.

15.4.2 If the system monitoring compound recoveries meet the acceptance criteria in the reanalyzed samples the samples are considered in control and the data may be reported.

15.4.3 If the system monitoring compound recoveries do not meet the acceptance criteria in the reanalyzed samples, then submit data from both analyses.

16.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up.

17.0 WASTE MANAGEMENT

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water and land by minimizing and controlling all release from hoods, and bench operations, complying with the letter and spirit of any waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

18.0 REFERENCES

Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), Massachusetts Department of Environmental Protection, January 1998.

19.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION FORMS

Table 8: Compound List and Reporting Limits for Target Polynuclear Aromatic Hydrocarbons

Analyte	Water (mg/L)	Soil (mg/Kg)
Naphthalene	0.005	0.5
2-Methylnaphthalene	0.005	0.5
Acenaphthylene	0.005	0.5
Acenaphthene	0.005	0.5
Fluorene	0.005	0.5
Phenanthrene	0.005	0.5
Anthracene	0.005	0.5
Fluoranthene	0.005	0.5
Pyrene	0.005	0.5
Benzo(a)anthracene	0.005	0.5
Chrysene	0.005	0.5
Benzo(b)fluoranthene	0.005	0.5
Benzo(k)fluoranthene	0.005	0.5
Benzo(a)pyrene	0.005	0.5
Indeno(123-cd)pyrene	0.005	0.5
Dibenz(ah)anthracene	0.005	0.5
Benzo(ghi)perylene	0.005	0.5

Table 9: Extractable Petroleum Hydrocarbon Totals

Analyte	**Water (mg/L)**	**Soil (mg/Kg)**
C_9 - C_{18}	0.030	3.0
C_{19} - C_{36}	0.040	4.0
C_{11} - C_{22}	0.085	8.5

Attached are form 1's for EPH soil and water analysis.

UNCONTROLLED COPY

METHOD: EPH_MA:AN
STANDARD OPERATING PROCEDURE
FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS – MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION

Applicable matrix or matrices: Soils, Waters
Standard Compound List and Reporting Limits: See Section 19.0

Approvals and Signatures

Laboratory Director:	Christopher A. Ouellette	Date:	8/8/00
QA Manager:	Kim B. Watson Kim B. Watson	Date:	8/8/00
GC Laboratory Manager	David Downing Dave Downing	Date:	8/8/00
Organic Technical Director:	Bryce E. Stearns	Date:	8/8/00

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of extractable aliphatic and aromatic hydrocarbons in water and soil extracts. The aliphatic hydrocarbons are quantitated as C_9 through C_{18} and C_{19} through C_{36} ranges. The aromatic hydrocarbons are quantitated in the C_{11} through C_{22} range. Individual polynuclear aromatic hydrocarbons (PAH) are also quantitated using this method.

Form 1

EXTRACTABLE PETROLEUM HYDROCARBON (EPH) ANALYSIS

Lab Name: SEVERN TRENT LABORATORIES
Lab Code: INCHVT
Matrix: WATER (soil/water)
Sample wt/vol: 1000.00 ML
% Moisture: 0 (%)
Extraction: SEPF
Extract Volume: 1 (ml)
Injection Volume: 1 (ul)
Conc. Units: MG/L

Contract: 98000
Case: 98000
SDG: 71575
Sample ID: EBLKH4
Sample ID: EBLKH4
Date Received: ______
Date Extracted: 11/23/98
Date Analyzed: 12/03/98
Dilution Factor: 1

CAS NO.	Analyte	Amount	Q	
91-20-3	Naphthalene	0.005	U	
91-57-6	2-Methylnaphthalene	0.005	U	
208-96-8	Acenaphthylene	0.005	U	
83-32-9	Acenaphthene	0.005	U	
86-73-7	Fluorene	0.005	U	
85-01-8	Phenanthrene	0.005	U	
120-12-7	Anthracene	0.005	U	
206-44-0	Fluoranthene	0.005	U	
129-00-0	Pyrene	0.005	U	
56-55-3	Benzo(a)anthracene	0.005	U	
218-01-9	Chrysene	0.005	U	
205-99-2	Benzo(b)fluoranthene	0.005	U	
207-08-9	Benzo(k)fluoranthene	0.005	U	
50-32-8	Benzo(a)pyrene	0.005	U	
193-39-5	Indeno(1,2,3-cd)pyrene	0.005	U	
53-70-3	Dibenzo(a,h)anthracene	0.005	U	
191-24-2	Benzo(ghi)perylene	0.005	U	

EPH Totals	Amount	Q
C9-C18 Aliphatics 1	0.030	U
C19-C36 Aliphatics 1	0.040	U
C11-C22 Aromatics 1,2	0.085	U

1- Hydrocarbon Range data exclude concentrations of any surrogate(s) and or internal standards eluting in that range.

2- C11-C22 Aromatic Hydrocarbons exclude the concentration of Target PAH Analytes

SAMPLE INFORMATION:

Matrix: Aqueous____ Soil____ Sediment____ Other ___
Containers: Satisfactory____ Broken ____ Leaking____
Aqueous Preservatives: N/A____ pH ≤ 2____ pH >2____
Temperature: Received on Ice____ Received at 4C____ Other____

Form 1

EXTRACTABLE PETROLEUM HYDROCARBON (EPH) ANALYSIS

Lab Name:	SEVERN TRENT LABORATORIES		Contract:	98004
Lab Code:	INCHVT		Case:	E0778
Matrix:	SOIL	(soil/water)	SDG:	71456
Sample wt/vol:	10.00	G	Sample ID:	EBLKG6
% Moisture:	0	(%)	Sample ID:	EBLKG6
Extraction:	SONC		Date Received:	
Extract Volume:	1	(ml)	Date Extracted:	11/18/98
Injection Volume:	1	(ul)	Date Analyzed:	12/03/98
Conc. Units:	MG/KG		Dilution Factor:	1

CAS NO.	Analyte	Amount	Q	
91-20-3	Naphthalene	0.5	U	
91-57-6	2-Methylnaphthalene	0.5	U	
208-96-8	Acenaphthylene	0.5	U	
83-32-9	Acenaphthene	0.5	U	
86-73-7	Fluorene	0.5	U	
85-01-8	Phenanthrene	0.5	U	
120-12-7	Anthracene	0.5	U	
206-44-0	Fluoranthene	0.5	U	
129-00-0	Pyrene	0.5	U	
56-55-3	Benzo(a)anthracene	0.5	U	
218-01-9	Chrysene	0.5	U	
205-99-2	Benzo(b)fluoranthene	0.5	U	
207-08-9	Benzo(k)fluoranthene	0.5	U	
50-32-8	Benzo(a)pyrene	0.5	U	
193-39-5	Indeno(1,2,3-cd)pyrene	0.5	U	
53-70-3	Dibenzo(a,h)anthracene	0.5	U	
191-24-2	Benzo(ghi)perylene	0.5	U	

EPH Totals	Amount	Q
C9-C18 Aliphatics 1	3.0	U
C19-C36 Aliphatics 1	4.0	U
C11-C22 Aromatics 1,2	8.5	U

1- Hydrocarbon Range data exclude concentrations of any surrogate(s) and or internal standards eluting in that range.

2- C11-C22 Aromatic Hydrocarbons exclude the concentration of Target PAH Analytes

SAMPLE INFORMATION:

Matrix: Aqueous_____ Soil_____ Sediment_____ Other_____
Containers: Satisfactory_____ Broken _____ Leaking_____
Aqueous Preservatives: N/A_____ pH ≤ 2_____ pH >2_____
Temperature: Received on Ice_____ Received at 4C_____ Other_____

03 November 1999

METHOD MAEPH - AROMATICS/ALIPHATICS
Water 1000ml to 1.0ml

Instrument: HP3012: DB5MS

COMPOUND	REP 1	REP 2	REP 3	REP 4	REP 5	REP 6	REP 7	Mean	TRUE	% R	STDev	MDL (mg/L)	RL	X
Naphthalene	0.0042	0.0043	0.0046	0.0043	0.0044	0.0042	0.0044	0.0043	0.0050	87	0.00013	0.00040	0.0050	12.5
2-Methylnaphthalene	0.0042	0.0044	0.0046	0.0042	0.0044	0.0042	0.0044	0.0043	0.0050	87	0.00015	0.00049	0.0050	10.3
Acenaphthylene	0.0042	0.0044	0.0047	0.0042	0.0044	0.0042	0.0043	0.0043	0.0050	87	0.00018	0.00058	0.0050	8.7
Acenaphthene	0.0042	0.0044	0.0046	0.0041	0.0044	0.0042	0.0044	0.0043	0.0050	87	0.00016	0.00049	0.0050	10.2
Fluorene	0.0045	0.0046	0.0050	0.0044	0.0046	0.0044	0.0046	0.0046	0.0050	91	0.00020	0.00063	0.0050	7.9
Phenanthrene	0.0044	0.0044	0.0049	0.0043	0.0046	0.0044	0.0046	0.0045	0.0050	90	0.00019	0.00059	0.0050	8.5
Anthracene	0.0044	0.0045	0.0049	0.0043	0.0046	0.0044	0.0046	0.0045	0.0050	91	0.00019	0.00061	0.0050	8.3
Fluoranthene	0.0043	0.0043	0.0048	0.0043	0.0045	0.0043	0.0045	0.0044	0.0050	89	0.00019	0.00060	0.0050	8.4
Pyrene	0.0042	0.0043	0.0048	0.0043	0.0045	0.0043	0.0044	0.0044	0.0050	88	0.00020	0.00063	0.0050	8.0
Benzo(a)anthracene	0.0040	0.0042	0.0046	0.0041	0.0044	0.0042	0.0043	0.0043	0.0050	85	0.00019	0.00059	0.0050	8.5
Chrysene	0.0041	0.0042	0.0046	0.0041	0.0043	0.0041	0.0044	0.0042	0.0050	85	0.00019	0.00059	0.0050	8.4
Benzo(b)fluoranthene	0.0048	0.0043	0.0048	0.0043	0.0046	0.0045	0.0046	0.0045	0.0050	91	0.00020	0.00063	0.0050	7.9
Benzo(k)fluoranthene	0.0031	0.0039	0.0041	0.0035	0.0037	0.0034	0.0037	0.0036	0.0050	73	0.00035	0.00109	0.0050	4.6
Benzo(a)pyrene	0.0039	0.0040	0.0044	0.0039	0.0041	0.0039	0.0041	0.0041	0.0050	81	0.00017	0.00054	0.0050	9.2
Indeno(1,2,3-cd)pyrene	0.0040	0.0041	0.0044	0.0039	0.0042	0.0039	0.0040	0.0041	0.0050	82	0.00016	0.00050	0.0050	10.1
Dibenzo(a,h)anthracene	0.0036	0.0039	0.0040	0.0035	0.0038	0.0036	0.0038	0.0037	0.0050	75	0.00018	0.00055	0.0050	9.0
Benzo(ghi)perylene	0.0037	0.0039	0.0042	0.0037	0.0040	0.0037	0.0039	0.0039	0.0050	78	0.00018	0.00058	0.0050	8.7
C11-C22 Aromatic EPH	0.0698	0.0721	0.0779	0.0694	0.0733	0.0699	0.0731	0.0722	0.085	85	0.0030	0.00938	0.085	9.1
C9-C18 Aliphatic EPH	0.0199	0.0238	0.0202	0.0236	0.0223	0.0174	0.0239	0.0216	0.030	72	0.0025	0.00782	0.030	3.8
C19-C36 Aliphatic EPH	0.0271	0.0320	0.0294	0.0338	0.0323	0.0230	0.0358	0.0305	0.040	76	0.0043	0.01367	0.040	2.9

%R = (70%-130%)

X=TRUE/MDL

MDL by: MRV 09/22/99
Reviewed by: WBR 11/03/99
Water extraction method: Separatory Funnel
Date extracted 08/25/99

METHOD MAEPH - AROMATICS/ALIPHATICS

Soil 10gm to 1.0 ml

03 November 1999

Instrument: HP3012: DB5MS

COMPOUND	REP 1	REP 2	REP 3	REP 4	REP 5	REP 6	REP 7	Mean	TRUE	% R	STDev	MDL (mg/Kg)	RL	X
Naphthalene	0.387	0.469	0.503	0.500	0.452	0.692	0.498	0.50	0.50	100	0.094	0.295	0.50	1.7
2-Methylnaphthalene	0.384	0.460	0.498	0.502	0.451	0.685	0.494	0.50	0.50	99	0.093	0.292	0.50	1.7
Acenaphthylene	0.368	0.451	0.483	0.491	0.435	0.667	0.484	0.48	0.50	97	0.092	0.288	0.50	1.7
Acenaphthene	0.374	0.453	0.485	0.497	0.440	0.681	0.489	0.49	0.50	98	0.095	0.298	0.50	1.7
Fluorene	0.392	0.449	0.514	0.491	0.462	0.707	0.508	0.50	0.50	101	0.099	0.311	0.50	1.6
Phenanthrene	0.380	0.460	0.496	0.497	0.451	0.706	0.502	0.50	0.50	100	0.101	0.317	0.50	1.6
Anthracene	0.362	0.451	0.497	0.498	0.442	0.686	0.479	0.49	0.50	98	0.099	0.311	0.50	1.6
Fluoranthene	0.376	0.462	0.493	0.494	0.441	0.709	0.488	0.49	0.50	99	0.103	0.325	0.50	1.5
Pyrene	0.371	0.454	0.494	0.489	0.434	0.711	0.481	0.49	0.50	98	0.106	0.333	0.50	1.5
Benzo(a)anthracene	0.356	0.437	0.476	0.461	0.424	0.686	0.461	0.47	0.50	94	0.103	0.322	0.50	1.6
Chrysene	0.352	0.449	0.475	0.476	0.409	0.696	0.460	0.47	0.50	95	0.107	0.338	0.50	1.5
Benzo(b)fluoranthene	0.393	0.476	0.487	0.536	0.465	0.712	0.532	0.51	0.50	103	0.099	0.312	0.50	1.6
Benzo(k)fluoranthene	0.294	0.402	0.49	0.448	0.350	0.653	0.367	0.43	0.50	86	0.118	0.370	0.50	1.4
Benzo(a)pyrene	0.317	0.400	0.446	0.448	0.390	0.627	0.415	0.43	0.50	87	0.096	0.300	0.50	1.7
Indeno(1,2,3-cd)pyrene	0.349	0.428	0.471	0.461	0.399	0.671	0.454	0.46	0.50	92	0.101	0.319	0.50	1.6
Dibenzo(a,h)anthracene	0.309	0.396	0.433	0.438	0.372	0.651	0.438	0.43	0.50	87	0.106	0.335	0.50	1.5
Benzo(ghi)perylene	0.320	0.414	0.443	0.439	0.384	0.66	0.436	0.44	0.50	88	0.105	0.331	0.50	1.5
C11-C22 Aromatic EPH	6.09	7.51	8.18	8.17	7.20	11.6	7.99	8.11	8.5	95	1.706	5.363	8.5	1.6
C9-C18 Aliphatic EPH	2.39	2.43	2.58	2.35	2.27	3.55	2.52	2.58	3.0	86	0.438	1.377	3.0	2.2
C19-C36 Aliphatic EPH	3.08	3.05	3.30	3.02	2.79	4.92	3.14	3.33	4.0	83	0.718	2.257	4.0	1.8

%R = (70%-130%)

X=TRUE/MDL

MDL by: MRV 09/22/99
Reviewed by: WBR 11/03/99
Soil extraction method: Sonication
Date extracted 08/25/99

APPENDIX A-90

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF INORGANIC IONS BY ION CHROMATOGRAPHY

STANDARD OPERATING PROCEDURE
FOR
THE DETERMINATION OF INORGANIC IONS BY ION CHROMATOGRAPHY

Applicable matrix or matrices: Water/Soil
Standard Compound List and Reporting Limits: See section 1.3

Approvals and Signatures

Laboratory Director: Michael F. Wheeler, Ph.D. Date: 10/24/02

QA Manager: Kirstin L. McCraken Date: 10/25/02

Inorganic Technical Director: Kristine A. Dusablon Date: 10/25/02

Metals Supervisor: William S. Cicero Date: 10/25/02

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of the anions listed in 1.2 for drinking water, surface water, ground water, mixed domestic and industrial wastes, soils and sediments. Per client request STL Burlington has performed this method on soil samples. Soil samples are analyzed after a 1:1 extraction using equal volumes of reagent water and the sample. The extracted liquid is then analyzed according to this method.

1.2 The procedure is applicable to the following inorganic anions: fluoride, chloride, bromide, nitrate-N, orthophosphate-P, and sulfate.

1.3 The reporting limit for the above anions is 0.20 mg/L for aqueous samples and 0.20mg/Kg for soil samples.

2.0 SUMMARY OF METHOD

2.1 A small volume of sample is introduced into an ion chromatograph, injected into a stream of carbonate/bicarbonate eluent, and passed through a series of anion exchangers. The anions of interest are separated by their relative affinities for a low capacity, strongly basic anion exchanger (guard and separatory columns). The separated anions are directed through a micromembrane suppressor bathed in continuously flowing, strongly acidic regenerant solution. The separated ions are converted to their highly conductive acid forms and the carbonate/bicarbonate eluent is converted to weakly conductive carbonic acid. The separated anions in their acid forms are measured by conductivity and are identified by their retention times as compared to a known standard. Target quantitation is performed by measurement of peak area in comparison to the calibration curve generated by known standards.

2.2 This procedure is based on EPA Method 300.0 and SW-846 Method 9056.

3.0 DEFINITIONS

3.1 Accuracy: the degree of agreement between a measurement and the true or expected value, or between the average of a number of measurements and the true or expected value.

3.2 Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of a similar matrix, meeting the above mentioned criteria.

3.3 Calibration: the establishment of an analytical curve based on the absorbance, emission intensity or other measured characteristic of known standard.

3.4 Calibration Blank (ICB/CCB): a volume of reagent water acidified with the same acid matrix as in the calibration standards.

3.5 Calibration Standards: a series of known standard solutions used to calibrate the instrument response with respect to analyte concentration.

3.6 Continuing Calibration Verification (CCV): a prepared standard solution used to verify the stability of the instrument calibration and instrument performance during the analysis of samples.

3.7 Corrective Action: action taken to eliminate the causes of an existing non-conformance, defect or other undesirable situation in order to prevent recurrence.

3.8 Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

3.9 Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

3.10 Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

3.11 Initial Calibration Verification (ICV): A prepared standard solution from a source separate from that of the calibration standards used to verify the concentration of the calibration standards and the adequacy of instrument calibration.

3.12 Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

3.13 Matrix: the substrate of a test sample.

3.14 Matrix Duplicate (DP): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate; Laboratory Duplicate.

3.15 Matrix Spike (MS): field sample to which a known amount of target analyte(s) is added.

3.16 Matrix Spike Duplicate (MSD): a replicate matrix spike.

3.17 Method Blank: a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

3.18 Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which the relative uncertainty is +100%. The MDL represents a range where qualitative detection occurs using a specific method. Quantitative results are not produced in this range.

3.19 Percent Solids (%S): the proportion of solid in a soil sample.

3.20 Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical and/or biological integrity of the sample.

3.21 Quality Control Sample: a control sample, generated at the laboratory or in the field, or obtained from an independent source, used to monitor a specific element in the sampling and/or testing process.

3.22 Low Level Standard (LLS): A solution prepared from the calibration standard stocks containing all of the analytes. The standard is analyzed at two times the reproting limit, to show the sensitivity of the lower end of the curve.

4.0 INTERFERENCES

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2 Using an AS14 column and guard column can usually eliminate the water dip or negative peak that elutes near and can interfere with the fluoride peak.

4.3 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.4 Carbonate and other small organic anions cause known co-elution. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

5.0 SAFETY

5.1 The toxicity or carcinogenity of each chemical used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be minimized as reasonably possible. A reference file of Material Safety Data Sheets (MSDS) for this test method is available to all personnel and must be read prior to performing this procedure. All laboratory personnel must be familiar with the laboratory environmental health and safety plan described in the STL Corporate Safety Manual (CSM).

6.0 EQUIPMENT AND SUPPLIES

6.1 Dionex DX500 with CD-20 conductivity detector

6.2 GP40 Gradient Pump and AS40 Automated Sampler

6.3 Anion Self-Regenerating Suppressor (ASRS-11) and AS14 column and guard column are used.

6.4 5mL Sample vials and tops.

7.0 REAGENTS AND STANDARDS

Sodium Carbonate Working Stock (10mM): Weigh 2.12g Na_2CO_3 into 2000mL volumetric flask and bring to a total volume of 2 Liters. Shake well, and allow all crystals to dissolve.

Sodium Bicarbonate Working Stock (10mM): Weigh 1.68g $NaHCO_3$ into a 2000mL volumetric flask and bring to a total volume of 2 Liters. Shake well, and allow all crystals to dissolve.

Combined Standard Stock Solution (Curve Stock Solution): To prepare the stock solution, weigh the following reagents into a 1000 ml volumetric flask:

Reagent:	Anion:	Weight (g)
(NaF)	Fluoride	0.2210g
(NaCl)	Chloride	0.1648g
(NaBr)	Bromide	0.1288g
(KNO_3)	Nitrate-N	0.1631g
(KH_2PO_4)	Orthophosphate-P	0.1834g
(Na_2SO_4)	Sulfate	0.1814g

Bring solution to 1000mL volume, and mix well. Allow all reagents to dissolve before use. This has now produced a Combined Standard Stock Solution. Solution must be stored in a polyethylene bottle.

Combined ICV/CCV Standard Stock Solution: To prepare the ICV/CCV stock solution, weigh the following reagents into a 1000 ml volumetric flask:

Reagent:	Anion:	Weight (g):	True Value (mg/L):
(NaF)	Fluoride	0.2210g	1.0
(NaCl)	Chloride	0.8242g	5.0
(NaBr)	Bromide	0.1489g	1.0
(KNO_3)	Nitrate-N	0.4892g	3.0
(KH_2PO_4)	Orthophosphate-P	0.2866g	2.0
(Na_2SO_4)	Sulfate	0.1.4786g	10.0

Bring solution to 1000mL volume with reagent water. Allow all reagents to go into solution before use.

Note: This solution must be prepared from different sources than those used for the Standard Stocks. Be sure to record all sources and lot numbers in the Standards Notebook.

ICV/CCV Working Solution: Pipet 5mLs of the ICV/CCV Stock solution into a 500mL volumetric flask. Bring up to volume with reagent water. The true value for each anion in this solution, are as follows:

Anion:	True Value (mg/L):
Fluoride	1.0
Chloride	5.0
Bromide	1.0
Nitrate-N	3.0
Orthophosphate-P	2.0
Sulfate	10.0

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 A minimum sample volume of 100 mL should be collected in plastic or glass bottles. If soil analysis has been requested, sample should be collected in a 250mL glass amber bottle. Immediately following collection, the samples should be cooled to 4°C (±2°C) and maintained at that temperature until the time of analysis.

8.2 The holding time for inorganic anions nitrate-N and orthophosphate-P is 48 hours from collection and 28 days from collection for all other anions.

8.3 Samples are stored from the time of receipt in the laboratory until 60 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or client-specific protocol, samples are disposed of after 60 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

9.1 Matrix Spike (MS)

Matrix spikes are analyzed at a frequency of one per 20 samples per site-specific matrix. The MS is used to provide information to the client about the effect of a site-specific matrix on the analytical procedure. The percent recovery of the MS should be within the established accuracy and precision limits.

9.2 Matrix Duplicate (DP)

A sample duplicate is analyzed at a frequency of one per 20 samples per site-specific matrix. The relative percent difference (%RPD) between the results of duplicate samples should be with ≤20%.

9.3 Instrument Performance Checks

Instrument performance is checked on a continuing basis using calibration blanks and calibrations standards following each calibration routine (ICV, ICB), after every ten analyses and at the end of the run (CCB, CCV). The results of the checks indicate if the calibration is still valid and that the system is free of contaminants. If the calibration is not confirmed within the specified limit for the ICV, then the instrument must be recalibrated. If the continuing calibration checks are not confirmed, then the samples bracketed by the failing standard must be reanalyzed.

Initial Calibration Verification (ICV)

The ICV standard is obtained from a source independent than the calibration standards and is used to verify the accuracy of the initial calibration. If client has not requested a MS/DP, then an ICVD will be analyzed. The concentration of the ICV and ICVD solution should be at or near the midpoint of the linear range of the calibration curve and should include every analyte for each mass used to report results. The percent recovery of the ICV and ICVD standard must be ± 10% of the true value.

Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

A calibration blank is analyzed immediately following every ICV and CCV, and at the beginning and end of each analytical run. The concentration of the ICB/CCB must be less than the established reporting limit.

Continuing Calibration Verification (CCV)
The CCV standard is analyzed at a frequency of every ten samples. The analyte concentration of the CCV is the same as for the ICV, and is typically at a concentration near the midpoint of the calibration curve. The percent recovery of the CCV must be ± 10% of the true value.

Low-Level Standard (LLS): The LLS is analyzed at the beginning of every analytical batch. The LLS provides verification that the instrument can detect low level anions. The percent recovery of the LLS must be 75-125%.

10.0 CALIBRATION AND STANDARDIZATION

For each anion of interest, prepare calibration standards at 8 concentration levels and a blank by adding measured volumes of one or more stock standards to a Teflon volumetric flask reserved for this purpose and dilute to volume with reagent water (See Table 1).

Table 1: Working Calibration Concentration

Working Level	Standard Concentration (mg/L)	Standard Volume (g)	Reagent Water (g)	Final Concentration (mg/L)
Calibration Blank	NA	NA	100g	NA
Calibration Level 1	2.0	10.0	100g	0.200
Calibration Level 2	5.0	10.0	100g	0.500
Calibration Level 3	100	1.00	100g	1.00
Calibration Level 4	100	2.50	100g	2.50
Calibration Level 5	100	5.00	100g	5.00
Calibration Level 6	100	10.0	100g	10.0
Calibration Level 7	100	15.0	100g	15.0
Calibration Level 8	100	20.0	100g	20.0

Tabulate the peak area response against the concentration. Using linear regression, calculate a correlation coefficient (r). The correlation coefficient must be ≥ 0.995 for the calibration to be considered acceptable. If this criterion is not met, the calibration procedure must be repeated prior to further analysis. The calibration curve of the ion chromatograph is established twice and when the results of the continuing calibration verification standard (CCV) indicate that the calibration relationship is no longer valid, whichever is more frequent.

11.0 PROCEDURE

11.1 Obtain the samples from sample management and allow the samples to come to room temperature.

11.3 Sample Preparation

For Aqueous Samples:
Pour approximately 5mLs of the sample into a vial reserved for IC analysis. Place the black cap on the vial, and insert into the appropriate place in the sample tray.

For Soil Samples:
Mix an equal part of the soil sample to reagant water (1:1 extraction). After sample has settled, pipet off the aqueous extract. Pour approximately 5mLs of the extract into a vial reserved for this analysis, and insert into the appropriate place in the sample tray.

ICV/CCV:
Pour approximately 5mLs of the QC standard into a vial reserved for IC analysis. Place in the appropriate spot in the sample tray.

LLS:
Pipet 1mL of the 100mg/L Combined Standard Stock Solution into a 250mL volumetric flask. Bring to volume with reagent water. LLS concentration is 0.40mg/L. Place in the appropriate spot in the sample tray.

ICB/CCB:
Pour approximately 5mLs of reagent water into a vial reserved for IC analysis. Place in the appropriate spot in the sample tray.

11.4 Instrument Operating Conditions & Analysis Sequence

Turn on the nitrogen gas and open the valves to eluent bottles A (sodium carbonate), B (sodium bicarbonate) and C (reagent water). Method AS14b has been set so that the eluent mixture is 32% Solution A, 18% Solution B, and 50% Solution C. This can be confirmed by loading the method.

Turn on the instrument by selecting from the main menu, **RUN, FILE**, and **Load Method**. Select the **"testing"** file.

Allow the IC to warm-up for approximately 30 minutes.

Create a sequence log by selecting from the main menu, **Schedule, and New**. Type in the analytical sequence, enter "STOP" in the last cell after the closing check standards, and enter "STOP" in the next two cells to ensure that the instrument will cease the run when at the end of the analytical sequence. An example analytical sequence is given below:

ICV
ICB
LLS
Nine Injections
CCV
CCB
Ten Injections
CCV (Closing Check Standard)
CCB (Closing Check Standard)

In the second column of the sequence log entitled "METHOD", type **"AS14b.met"** in each cell that corresponds to a sample or QC items that will be analyzed. In the next column type the file name. The naming convention for the filename is the date of analysis and a sequential alpha characterization, AA for the first run of the day, BB for the second, and so on. For example, the filename for the first analytical run that started on October 10, 2002 would be 101002AA. After this information is entered, select **FILE** then select **SAVE AS**, and type the designated filename.

Print two copies of the sequence log. Attach one copy of the sequence log to the ETR Worksheet and staple the other into the IC run log notebook.

Before beginning analysis, record the current instrument conditions (conductivity and PS) in the instrument run log notebook designated for this purpose.

11.5 Analysis

Place the sample vials into the auto sampler cartridges in same order as the analytical sequence. Ensure that the black dots on the cartridge are on the right and place the cartridges into the auto sampler. Place in front of the spring-loaded arm.

Press LOAD/RUN button on the instrument to initiate analysis, then select the **black** arrow (▶)on the PC connected to the instrument, select "YES" from the prompt message.

After the sequence is complete, review the results against the performance criteria given in section 9.0. Samples with target concentrations that exceed the linear range of the calibration curve must be diluted and reanalzyed. Quantitative results should be reported in appropriate units and significant figures and must be corrected for dilutions and percent solids.

Dionex PeakNet software is used for data acquisition, processing and quantitaion.

12.0 CALCULATIONS

12.1 Percent Recovery (Accuracy)

$$(\%R) = \frac{SR}{SA} * 100$$

Where:
SR = Sample Result
SA = Spike Added (concentration)

12.2 Matrix Spike Percent Recovery

$$MSRecovery(\%) = \frac{SSR - SR}{SA} * 100$$

Where:
SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

12.3 Relative Percent Difference (%RPD)
Where:

$$\%RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

D_1 = Original Sample Value
D_2= Replicate Sample Value

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Review the samples, standards and QC samples against the performance criteria given in section 9.0 for Quality Control. If the results do not fall within the established limits or criteria, corrective action is required. A QC Summary is provided in Section 17.0, Table 1, along with recommended corrective actions for each test method. If corrective action is not taken or unsuccessful, the situation should be documented and reported in the project narrative. All data that does not meet established criteria must be flagged with the appropriate data qualifier and noted in the project narrative.

14.0 METHOD PERFORMANCE

14.1 An Initial Demonstration of Capability is required for each analyst before unsupervised performance of this method.

14.2 An Initial Method Detection Limit (MDL) determination for each test method referenced in this SOP is performed following the procedure described in the reference method, 40CFR, Part 136, Appendix B and laboratory SOP LP-LB-009. The MDL is verified or repeated when a significant change to the method occurs. Significant changes include the use of alternate reagents or standard reference materials, new instrumentation or the use of alternate sample preparation procedures.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 The laboratory optimizes technology to minimize pollution and reduce the production of hazardous waste whenever possible.

15.2 The laboratory procedures for waste management comply with applicable federal, state and local regulations and are described in SOP LP-LB-001HAZWD.

16.0 REFERENCES

16.1 *Test Methods for Evaluating Solid Waste Physical/Chemical Methods* (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

16.2 *Methods for Chemical Analysis of Water and Wastes*, USEPA EPA-600/4-79-020 Revised March 1983, Method 300.0

17.0 TABLES, DIAGRAMS, FLOWCHARTS

17.1 Table1: *QC Summary and Recommended Corrective Action*

Table 2: QC Summary & Recommended Corrective Action

QC Item	Frequency	Acceptance	Recommended Corrective Action*
ICAL Blank + 8 Standards	As Required	Correlation Coefficient <0.995	System Check, Reanalyze
ICV	Each Analytical Batch	%R ± 10% of true value	System Check, Reanalyze, Prepare new standard solutions, Recalibrate, Reanalyze
CCV	After every 10 samples and end of analytical batch	%R ± 10% of true value	System Check, Recalibrate. Reanalyze any samples not bracketed by acceptable CCV.
ICB/CCB	Following each ICV/CCV	Target < RL	System Check, Recalibrate
Low Level Standard	Following the ICV	%R ± 25% of true value	System Check, Recalibrate
Matrix Spike	With every 20 field samples or as needed	%R (75-125)	Note in Project Narrative
Sample Duplicate	With every 20 field samples or as needed	%RPD ± 20% of original sample determination	Note in Project Narrative

**The recommended corrective action may include some or all of the items listed in this column. The analyst must use professional judgement to investigate and correct problems before proceeding with analysis. Suspect data must be qualified and reported in the project narrative.*

APPENDIX A-91

METHOD 150.1/9040B/9045C
STANDARD OPERATING PROCEDURE FOR pH

METHOD 150.1 / 9040B / 9045C
STANDARD OPERATING PROCEDURE FOR pH

Applicable Matrix or Matrices: Soil/Water
Standard Compound List and Reporting Limits: N/A

Approvals and Signatures

Laboratory Director: Christopher A. Ouellette

QA Manager: Kim B. Watson
Kim B. Watson

Inorganic Manager: Kristine Dusablon
Kristine A. Dusablon

Inorganic Supervisor William S. Cicero

Wet Chemistry Coordinator: Alicia M. Johnson

1.0 SCOPE AND APPLICATION

1.0 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition). Wastes may be solids, sludges, or non-aqueous liquids.

2.0 SUMMARY OF METHOD

2.0 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. Samples which have water present in less than 20% of the total volume of sample, are mixed with reagent water and the pH of the resulting aqueous solution is measured.

3.0 DEFINITIONS

3.1 pH: the intensity factor of acidity ($-\log[H^+]$), or activity of the hydrogen ion.

4.0 INTERFERENCES

4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.

4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.

4.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1:9) may be necessary to remove any remaining film.

4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 STL Burlington maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. STL Burlington also has a written environmental health and safety plan.

5.3 Please note chemicals that have the potential to be highly toxic or hazardous, the appropriate MSDS must be reviewed by the employee before handling the chemical.

6.0 EQUIPMENT AND SUPPLIES

6.1 All pH measurements are performed on the Beckman 45 pH meter.

6.2 Magnetic stirrer and Teflon-coated stirring bar.

6.3 Thermometer or temperature sensor for automatic compensation.

7.0 REAGENTS AND STANDARDS

7.1 Standard buffer solutions available from commercial vendors: pH 4, 6, 7 and 10 buffer solutions are necessary.

7.2 Occasionally, it is necessary to prepare pH standards to bracket a sample with a pH of less than 4.00 or greater than 10. These are prepared as follows:

7.2.1 <u>pH 1 standard:</u> 67 mL 0.2M HCl and 25 mL 0.2 M KCl plus nanopure H_2O to 100 mL.

7.2.2 <u>pH 2 standard:</u> 6.5 mL 0.2M HCl and 25 mL 0.2 M KCl plus nanopure H_2O to 100 mL.

7.2.3 <u>pH 13 standard:</u> 66.0 mL 0.2M NaOH and 25 mL 0.2 M KCl plus nanopure H_2O to 100 mL.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.

8.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.

9.0 QUALITY CONTROL

9.1 A pH 6 check standard is used every ten samples. The measured pH must be within 0.05 pH units of the true value.

9.2 Samples greater than pH 8.30, but less than pH 10, require analyzing the pH 10 standard buffer. The measured pH must be within 0.05 pH units of the true value.

9.3 Samples less than pH 4 or greater than pH 10 require the preparation of an appropriate standard using 2.2 M KCl and either 0.2 M HCl or 0.2 M NaOH (see section 7.0). The measured pH must be within 0.05 pH units of the true value.

9.4 A DI Water Blank is only analyzed prior to soil sample analysis. The pH of the DI Water Blank must be between pH 6.00 and pH 7.00.

Note: Samples must be qualified with a standard pH buffer greater than, and less than the sample pH.

10.0 CALIBRATION AND STANDARDIZATION

10.1 The electrode is stored immersed in pH 7 buffer. Be sure to remove the rubber plug attached to the electrode prior to use. Also, check that the level of saturated KCl is not more than 1 inch below the vent hole.

10.2 Now immerse the electrode in fresh pH 7 Standard Buffer and press the Calibrate Button. This pH meter is programmed to "recognize" several different Standard Buffers, and should quickly begin flashing "7.00" for "Standard 1". When the measurement has stabilized, the instrument will beep, the "eye" symbol will appear, and the readout will freeze. Immediately press the calibrate button a second time and wait for the beep.

10.3 Immerse electrode in pH 4 Standard Buffer for 15-30 seconds. Replace with fresh pH 4 Buffer and after 15-30 seconds, press the calibrate button. Again, repeat immediately.

10.4 Once the pH meter has been calibrated, verify calibration with pH 6 Standard Buffer. Do not press the calibrate button; instead, use the "pH" button directly below it. The accepted range for this buffer is 5.97-6.03. If the result falls outside this range, repeat the calibration procedure until the pH 6 Check Standard passes.

11.0 PROCEDURE

11.1 Standardize the meter and electrode system as outlined in Section 7.0.

11.2 Analyze samples as follows:

11.2.1 Any aqueous sample, or multiphasic sample where the aqueous phase constitutes at least 20% of the total volume, may be measured directly. Samples must be analyzed as soon as possible, but should be allowed to reach room temperature first.

11.2.2 Solid samples may be analyzed by accurately weighing 15-20 g of sample into a clean, dry beaker, then adding an equal gram weight of nanopure H_2O. Sample and water should be mixed and allowed to stand for 30 minutes. When measuring pH, do not use a stir bar (for these samples) and do not bury the electrode in the solid component. An ash or extremely powdery sample may require the addition of more nanopure H_2O to produce a mixture of measurable consistency. If required, note the volume of water actually added.

11.3 Now analyze all samples. Remember to include the pH 6 Check Standard every ten samples. Should any sample fall below pH 4.00 or above 8.30, additional check standards must be run. Samples greater than 8.30, but less than 10, require analyzing the prepared pH 10 Standard Buffer. Samples less than 4.00 or greater than 10 require the preparation of an appropriate standard using 0.2 M KCl and either 0.2 M HCl or 0.2 M NaOH. The formulas for these standards are provided in the reagent section.

11.3.1 Do not recalibrate the meter, simply analyze the check standard and report the result. However, the result must be ±0.1 of the true value or the meter must be recalibrated.

12.0 CALCULATIONS

12.1 Report all pH results to 0.01 units.

13.0 METHOD PERFORMANCE

13.1 In a single laboratory (EMSL), using surface water samples at an average pH of 7.7, the standard deviation was ± 0.1. A precision of 0.1 pH unit should be attainable in the range of pH 6.0 to 8.0. No data is provided for method performance for Method 9045C.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the USEPA recommends recycling as the next best option.

14.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.0 DATA ASSESSMENT, CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Data is initially reviewed by the analyst in the lab and stamped as such. Following this, QC personnel secondarily review the data before being put into its final data package form where the data is thirdly reviewed before being sent to the client.

15.2 Data that is out of control is marked as such and slated for re-analysis. Any corrective action undertaken is documented on a corrective action form (detailing the client information, problem, investigation findings and solution). This form is kept together with the project.

16.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

16.1 Generally any data that is out of control is considered unusable. There are however, cases in which the laboratory supervisor will be made aware of the issue, and if the data is used it will be thoroughly narrative noted.

17.0 WASTE MANAGEMENT

17.1 The USEPA requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the Waste Management Manual for Laboratory Personnel, available from the American Chemical Society at the address listed in Section 14.3.

18.0 REFERENCES

18.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

18.2 EPA Methods and Guidance for the Analysis of Water, Office of Water, Method No. 150.1 (1997).

19.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION FORMS

19.1 Analysis Logbook Form PH1B

Analyst:_______________

Date:_______________

Time:_______________

Sample #	**If Soil 1:1 Sample/ DIH$_2$O Slurry**	**pH**

Calibration Standards:

pH 4:__________

pH 7:__________

Check Standards:

pH 2:__________

pH 6:__________

pH 10:_________

pH 13:_________

Standard Buffer Solutions:

	Lot #	Tag #
pH 4:		
pH 6:		
pH 7:		
pH 10:		

pH 1 Lot #:_______________

pH 2 Lot #:_______________

pH 13 Lot #:_______________

DI Water Blank (for soils only)

____

APPENDIX A-92

METHOD TPH GAS (8015-GAS) STANDARD OPERATING PROCEDURE FOR THE TOTAL PETROLEUM HYDROCARBONS AS GASOLINE

METHOD TPH GAS (8015_GAS)
STANDARD OPERATING PROCEDURE
FOR TOTAL PETROLEUM HYDROCARBONS AS GASOLINE

Applicable matrix or matrices: water, soil.

Approvals and Signatures

Laboratory Director: Christopher A. Ouellette

QA Manager: Kim B. Watson
Kim B. Watson

Organics Manager: Bryce E. Stearns

1.0 Scope and Application

1.1 This method describes the procedures used in the analysis of soil and water samples for gasoline and gasoline range organics (GROs). GROs correspond to the range of alkanes from C6 to C10 and covering a boiling point range of approximately 60°C - 220°C

1.2 The typical reporting limits for water samples is 0.05 mg/l and 0.5 mg/kg for soil samples.

2.0 Summary of Method

2.1 The analysis of samples is performed with the intent of meeting quality control requirements of The California State LUFT method

2.2 Prior to sample analysis, the instrumentation is calibrated using a five point calibration curve for gasoline. Instrument stability is verified every ten sample analyses with the mid-point gasoline standard.

2.3 The analysis instrumentation consists of a purge and trap unit and gas chromatograph equipped with a flame ionization detector.

3.0 Definitions

3.0 ANALYTICAL BATCH - A group of field samples with similar matrices that are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.1 CALIBRATION STANDARD (CAL) - A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.2 CONTINUING CALIBRATION VERIFICATION (CCV) - An analytical standard containing all target analytes, surrogate and internal standard compounds that is used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.3 INITIAL CALIBRATION VERIFICATION (ICV) - An analytical standard containing all target analytes, surrogate and internal standard compounds that are prepared from a source external to the laboratory and different from the supplier of the initial calibration standards. The purpose of the ICV is to verify that the initial calibration is in control.

3.4 LABORATORY CONTROL SAMPLE (LCS) - The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

3.5 LABORATORY FORTIFIED SAMPLE MATRIX/SAMPLE MATRIX DUPLICATE (MS/MSD) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS/MSD is analyzed exactly like a sample. Its purpose is used to evaluate the accuracy and precision of the laboratory performance of the analytical method in a specific sample matrix.

3.6 METHOD BLANK (VBLK, similarly known as the LABORATORY REAGENT BLANK) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The VBLK is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.7 PRIMARY DILUTION STANDARD SOLUTION - A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.8 STOCK STANDARD SOLUTION - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.9 SURROGATE ANALYTE (SS) - Non-target analyte compounds that are similar in composition and behavior to the target analytes but are not expected to be found in environmental media (often, isotopically labeled target analytes are used for this purpose) and are added to every standard, quality control sample, and field sample at a known concentration prior to preparation and/or analysis. Surrogate responses are used to evaluate the accuracy of the laboratory's performance of the analytical method in a specific sample matrix.

3.10 TRIP BLANK - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the trip blank is to determine if method analytes or other interferences are present in the field environment.

4.0 Interferences

4.1 Samples may become contaminated by the diffusion of volatile organics through the vial septum. Methanol and water trip blanks should be analyzed to check for such contamination.

4.2 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary.

4.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. To reduce the potential for carryover, the sample purging device must be thoroughly rinsed between samples with an appropriate solvent. Purge and trap devices or headspace devices should be thoroughly baked out between samples. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are not present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

4.4 The laboratory where volatile analysis is performed should be completely free of solvents. The presence of organic solvents in the laboratory where volatile organics are analyzed will lead to random background levels and appropriate precautions must be taken to minimize this problem.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 STL Burlington maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. STL Burlington also has a written environmental health and safety plan.

5.3 Please note chemicals that have the potential to be highly toxic or hazardous, the appropriate MSDS must be reviewed by the employee before handling the chemical.

6.0 Equipment and Supplies

6.0 Gas Chromatograph: An analytical system equipped with a flame ionization detector. (HP5890 or equivalent.)

6.1 Purge and Trap: A sample concentrator able to purge both water and soil samples. (Dynotech model # PTA-30W/S or equivalent)

6.2 Data System: A data system capable of recording detector signal, reintegration and quantitation (Maxima 820 or equivalent).

6.3 Fused Silica Capillary Column: An HP-5 (30m x 0.53mm ID, 0.88mm film thickness) or equivalent.

6.4 GC Configuration: The purge and trap unit transfer line is directly connected to the analytical column.

6.5 GC Conditions: The following represent typical instrument configuration.

Initial Temperature	45 °C
Initial Time:	3.0 minutes
Rate #1:	3.0 °C/minutes
Temperature	50 C
Hold:	0 minutes
Rate #2:	30 °C /minute
Temperature:	220 °C
Hold:	5 minutes
Carrier Gas Flow:	15 ml/min.
FID Make-up:	15 ml/min.
FID hydrogen:	30 psi
FID Air:	300 psi

6.3 Purge and Trap Conditions

Purge Flow:	40mL/min.
Purge Time:	10.0 min.
Desorb Temperature:	250°C
Desorb Time:	0.5 min.
Bake Time:	8 min.
Bake Temperature:	260°C

7.0 Reagents and Standards

7.1 Solvents

7.1.1 Methanol - purge and trap grade.

7.2 Standards

7.2.1 The stock standard solutions are purchased as certified solutions at a concentration of 5 mg/mL unleaded gasoline.

7.2.2 Primary dilution standards are prepared from the purchased stock solution at a concentration of 500 mg/L. This solution also serves at the matrix spiking solution. Stock standards are stored in the freezer and brought to room temperature prior to using for preparation. Primary standards are also stored in the freezer for a maximum of thirty days from the date of preparation. Working standards are made on an as needed basis.

7.2.3 Five point calibration concentrations (µg/L).

Compound	Conc 1	Conc 2	Conc 3	Conc 4	Conc 5
Gasoline	50	100	200	500	1500
Bromofluorobenzene	200	200	200	200	200

7.2.2 Retention Time Standard - The following standard is used as a retention time marker.

Compound	Concentration (mg/L)
n-dodecane ($C_{12}H_{26}$))	25

7.2.3 Surrogate Standard

Compound
Bromofluorobenzene

40 ul of 25ppm surrogate is spiked into either 5 ml for water samples or 1.0 gram for soil samples.

7.2.4 Matrix Spike Standard - Amount spiked

Compound	Water (µg/L)	Soil (µg/Kg)
Gasoline	0.500	2.50

To achieve these concentrations 5 ul of 500 ppm MS solution is spiked into either 5 ml of water or 1.0 gram of soil.

8.0 Sample Collection, preservation, shipment and storage

8.1 Samples are preserved in a refrigerator at 4 ± 2°C.

8.2 Samples must be analyzed within 14 days of collection.

9.0 Quality Control Requirement

9.1 Calibration and Standardization

Prior to sample analysis a five point calibration for gasoline is analyzed. A typical calibration is as follows:

IBLK
50 ppb STD
100 ppb STD
200 ppb STD
500 ppb STD
1500 ppb STD
QCS
Dodecane 25 ppb
Method Blank
10 Samples
500 ppb Check STD
10 Samples
500 ppb Check STD
Method Blank
10 Samples
500 ppb Check STD

The initial calibration curve is prepared by spiking the gasoline standard into 5 ml reagent water and purging.

The initial calibration must have a correlation coefficient 0.995 using a linear fit. The response for surrogate compound BFB is determined from a single point based on the response in the 500 ppb STD.

9.2 Continuing Calibration - Mid Point Calibration Check

As indicated in the analytical sequence, the 500 ppb gasoline standard is used to check instrument stability.

9.2.1 The standard must be analyzed every 10 sample analyses.

In order to have compliant data, the check standard (initial) and closing must meet the following criteria:

9.2.1.1 The concentrations of the analytes in the continuing calibration check standard must be ± 15% D on the quantitation column.

$$\% \text{ Difference} = \frac{(\text{calculated - nominal})}{\text{nominal}} * 100$$

9.2.1.2 Retention time of the surrogate must fall within established windows using the mean retention time from the curve. The established retention time window is ± 0.11 minutes.

9.3 Retention Time Windows

9.3.1 The procedure recommended in SW-846 for the determination of retention time windows is as follows:

- Make three injections of all single component standard mixtures and multiresponse products (i.e. PCBs) throughout the course of a 72 hour period. Calculate the standard deviation of the three absolute retention times for each single component standard. For multiresponse products, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples. The retention time window is defined as ± 3 times the standard deviation of the absolute retention times for each standard. The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed.

9.4 It is the laboratories experience that the SW-846 procedure results in retention time windows that are very tight and that favor false negatives. This would result in analytes that are present in the sample to not be reported. SW-846 is a guidance document that encourages modifications based on laboratory expertise. For this reason the laboratory has taken a more conservative approach to the establishment of retention time windows.

9.4 Each analytical sequence is thoroughly reviewed and a retention time of ± 0.11 minutes from the mid-point standard for 0.32 mm ID columns is used for identification purposes. In addition, the laboratory will look at the retention time shift of the surrogates in each sample to see if further compensation of the retention time window is necessary. This routine, while more time consuming than the SW-846 approach prevents the laboratory from reporting false negatives.

9.5 An acceptable method blank cannot contain target analytes above one-half the reporting limit. . If the method blank exceeds these criteria, the analytical system may be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. If the method blank fails to meet the above requirements, professional judgement will be used to determine if the entire extraction batch needs to be re-analyzed or if re-analysis will occur on those samples that have target analytes detected.

11.0 Procedure

11.2 Water - 5 ml of sample is fortified with surrogate and analyzed. Samples requiring dilution analysis are prepared in a 5 ml syringe combining the appropriate amount of sample with reagent water and then adding the surrogate spike.

11.3 Low Level Soils - At least 1.0 gram of sample is added to the purge vessel. Five milliliters of reagent water fortified with surrogate is added to the purge vessel.

11.4 Medium Level Soils - Four grams of soil is extracted with 10 mls of methanol. Up to 100 ul of this methanol extract can be purged with 5 ml of reagent water fortified with surrogate

12.0 Calculations

12.1 A linear curve is used for quantitation of analytes

$$Y = a_o + (1/a_1) * x$$

Where:
y =concentration
x =peak height or area
a_o =intercept
$(1/a_1)$ =slope

12.2 From injected sample extract concentration the sample concentrations are calculated as follows:

Water Samples:

$$Sample\ Conc. \frac{(ug)}{L} = conc.purged \frac{(ug)}{L} * DF$$

DF= Dilution Factor

Soil Samples:

$$C_x(ug/Kg\ dry\ weight) = conc.\ purged\ (ug/L) * \frac{purge\ volume\ (L)}{spl.\ amount\ (Kg)} * \frac{100}{\%\ solids} * DF$$

DF= Dilution Factor

12.2 Identification

12.2.1 In general, gasoline fuel should elute before n-dodecane (C12). The fuel mixture shall fall 90 percent within the calibration standard range and exhibit a reasonable pattern match to be identified as gasoline. See Section 12.3 for qualifiers.

12.3 The following qualifiers are used to help identify the chromatographic pattern if it does not match gasoline.

Y - A fuel mixture pattern is detected, but the fuel mixture does not fall 90 percent within the calibration standard range and exhibit a reasonable pattern match to any of the calibrated mixtures.

Z - Unknown single peaks or chromatographic patterns are detected but do not resemble a typical fuel pattern.

Also, if fuel oil #2 is detected it must not be identified and reported as gasoline with qualifiers.

13.0 Method Performance

13.1 Precision and Accuracy

Laboratory precision and accuracy data were obtained for the method analytes using laboratory control spikes with analytes at concentrations of 125µg/Kg for solid and 0.25µg/L for aqueous matrices. Results were obtained using the analytical instrumentation described in section 6.

13.2 Method Detection Limit Study

This study is a statistically derived assessment of method performance with respect to the variance in the production of extracts and their analysis. Method detection limits are calculated using the formula (3):

$\text{MDL} = S\ t_{(n-1,\ 1\text{-alpha} = 0.99)}$

$t_{(n-1,\ 1\text{-alpha} = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates
S = the standard deviation of the replicate analyses

14.0 Pollution Performance

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.0 Data assessment and Acceptance criteria and Corrective actions for out of Control data.

15.1 Samples must meet technical acceptance criteria before reporting data.

15.1.1 Corrective action for failure to meet instrument performance checks, initial, continuing calibration and method blanks must be completed prior to sample analysis.

15.1.2 Corrective action for system monitoring compounds and internal standard compounds that fail to meet acceptance criteria must be completed prior to sample analysis.

15.2 If the surrogate monitoring compound recoveries fail to meet acceptance criteria:

- Check all calculations, instrument logs, the system monitoring compound and internal standard compound spiking solutions and the instrument operation. If the calculations were incorrect, correct calculations and verify that the system monitoring compound recoveries and internal standard compound responses meet acceptance criteria.
- If the instrument log for the amount of surrogate standard compound spiking solution which was added. If an incorrect amount was spiked reanalyze with the correct amount.
- Check the preparation of the surrogate standard compounds for concentration and expiration.
- Verify that the instrument is operation correctly.

15.4 Determine if the problem was a matrix effect.

15.4.1 Check the surrogate recoveries for the MS and MSD.

15.4.2 If the surrogate monitoring compound recoveries meet the acceptance criteria in the reanalyzed samples the samples are considered in control and the data may be reported.

15.4.3 If the surrogate monitoring compound do not meet the acceptance criteria in the reanalyzed samples, then submit data from both analyses.

15.5 Method Blank: A method blank is analyzed at the beginning of each analytical window of up to 20 samples. All analytes must be less than the quantitation limit.

15.6 Surrogate Standard: Method blanks and samples are fortified with surrogate before analysis begins. Surrogate compound and recovery limits are listed below.

Compound	Water (%R)	Soil (%R)

Bromofluorobenzene	75-125	75-125

If recovery of the surrogate compound is outside QC limits the sample must be reanalyzed.

15.7 Matrix Spike/Matrix Spike Duplicate(MS/MSD), Laboratory Control Sample (LCS). An MS/MSD analysis is required every 20 samples or sample delivery group (as specified by the client). The MS/MSD analysis consists of spiking two aliquots of the same sample with matrix spike prior to analysis.

The LCS is reagent water or blank pool sand spiked with matrix spike. The recovery limits are as follows (%):

Compound	MS/MSD (%R)	%RPD	LCS (%R)
Gasoline	70-130	30	75-125

16.0 Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Reports will be initiated in order to provide for investigation and follow-up.

16.2 If the QC limits for MS/MSD recovery are not met, then the LCS recovery shall be evaluated. If the QC limits are met in the blank spike, the MS/MSD recovery problem is identified as a matrix effect and no further action shall be required. If the QC limits for LCS recovery are not met, the situation is considered out of control and corrective action shall be taken. The affected samples shall be reanalyzed for purgeable analyses after the spike recovery problem has been corrected.

17.0 Waste Management

17.1 The USEPA requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in a an acceptable manner. The Agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

18.0 References

18.1 Standard Method for the Examination of Water and Wastewater, 19th edition; Eaton, A.D. Clesceri, L.S. Greenberg, A.E. Eds; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, D.C., 1995.

18.2 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

19.0 Tables, diagrams, flowcharts and validation data.

Table 1. Compound List and Reporting Limits

Compound	Water (mg/L)	Soil (mg/Kg)
Gasoline	0.050	0.50

The base quantitation limit is adjusted for medium level dilution and percent solids if applicable.

Table 2. Corrective Actions

Volatile Organics Method TPH - GAS			
Quality Control Criteria	Frequency	Acceptance	Corrective Action
5 point initial calibration (ICAL):	As Required	Correlation coefficient 0.995	Recalibrate, mix new standards, reanalyze
CCAL	Every 10 samples	± 15%	Re-shoot, check integrations, mix new std. Reanalyze ICAL
Method Blank	After Each CCAL	Targets < 1/2 Reporting Limit (0.025 µg/L, 0.25 µg/kg)	Reanalyze, check for contamination, correct as required
Samples	--	Concentrations below highest calibration standard (1500 µg/L)	Dilute and reanalyze samples that are more concentrated than the highest calibration standard (15000 µg/L)
Surrogates	Every sample, blank and QC sample must be spiked with surrogate	See control limits in SOP	Any sample with outages must be reanalyzed to confirm. Present both sets of data.
Matrix Spike/Matrix Spike Duplicate	1 set every 20 samples, Full compound list spike required	Comparable results for spike and duplicate	Evaluate LCS. If compounds failing in MS/MSD are acceptable in the LCS the outages will assume to be matrix related.
LCS	Once per 20 samples (full compound list; independent std)	See control limits in the SOP	Check Std., Check Quantitation, Evaluate MS/MSD. Reanalyze batch if failing compounds are present in the samples.

APPENDIX A-93

METHOD TPH EXTRACTABLES STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF TOTAL PETROLEUM HYDROCARBONS

METHOD TPH EXTRACTABLES
STANDARD OPERATING PROCEDURE
FOR THE ANALYTIS OF TOTAL PETROLEUM HYDROCARBONS

Applicable Matrix or Matrices: Water, Soil and Sediment
Standard Compound List and Reporting Limits: See Appendix A

Approvals and Signatures

Laboratory Director: Michael
Michael F. Wheeler, Ph.D.

QA Manager: Kirstin L. McCracken
Kirstin L. McCracken

Organics Technical Director:
Bryce E. Stearns

GC Manager:
Jennifer L. Clements

1.0 SCOPE AND APPLICATION

1.1 This method describes the procedures used to measure the concentration of total petroleum hydrocarbons (diesel and motor oil) in water and soil by gas chromatography (GC) analysis using a flame ionization detector (FID).

1.2 The method was written to support the quality control requirements of the California State LUFT Method.

2.0 SUMMARY OF METHOD

2.1 A sample extract submitted for TPH analysis is analyzed by a capillary column gas chromatograph equipped with a flame ionization detector. Prior to sample analysis, external standard calibration is performed using a minimum of five concentration levels for diesel and motor oil. Instrument stability is verified every ten samples with a mid-level calibration check standard.

2.2 Individual concentrations of target TPH analytes are calculated using a linear regression curve.

3.0 DEFINITIONS

3.1 Batch: environmental samples that are prepared and/or analyzed together with the same process using the same lot(s) of reagents. A preparation batch is composed of one to twenty field samples of the same matrix that meet the above criteria. An analytical batch is composed of prepared field samples, extracts, digestates or concentrates that are analyzed together as a group. An analytical batch can exceed 20 samples and is not limited to a specific matrix.

3.2 Holding Time: the maximum time that a sample can be held before preparation and/or analysis and still be considered valid as promulgated in the method.

3.3 Method Blank (PBLK): a blank matrix processed simultaneously with and under and the same conditions as field samples and carried through all steps of the analytical procedure to determine if method analytes or other interferences are present in the laboratory, reagents or equipment.

3.4 Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s), processed simultaneously with and under the same condition as field samples and carried through all steps of the analytical procedure.

3.5 Laboratory Control Sample Duplicate (LCSD); a replicate laboratory control sample. A quality control indicator that may be used to assess precision associated with laboratory procedures.

3.6 Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added in order to determine the contribution of matrix bias.

3.7 Matrix Spike Duplicate (MSD): replicate matrix spike and quality control indicator that may be used to assess matrix specific precision.

3.8 Matrix Duplicate: a duplicate aliquot of a sample processed and analyzed independently under the sample conditions as the field sample; also referred to as the sample duplicate or replicate.

3.9 Surrogate: a substance with properties that mimic the analyte of interest but are unlikely to be found in environmental samples.

3.10 Spike: a known mass of target analyte added to a blank sample used to determine recovery efficiency for quality control purposes. Used as a measure of accuracy.

3.11 Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations.

3.12 Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions conform to themselves.

3.13 Calibration: to determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument or other device. The levels of the applied calibrations standard should bracket the range of planned or expected sample measurements.

3.14 Calibration Standard: a substance or reference material used to calibrate an instrument.

3.15 Calibration Curve: the graphical relationship between the known values such as concentrations, of a series of calibration standards and their instrument response.

4.0 INTERFERENCES

4.1 Sources of interference in this method can be attributed to contaminated solvent, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of coeluting compounds in the sample matrix to which the FID will respond.

4.2 Matrix interference may be caused by contaminants co extracted with the sample that vary from source to source. Some samples may require extract cleanup in order to achieve desired degrees of discrimination and quantitation.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be minimized as reasonably possible. A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel.

5.2 Safety glasses, gloves and protective clothing (lab coat) must be worn while performing this method.

5.3 All laboratory personnel must be familiar with the laboratory environmental health and safety plan described in the STL Corporate Safety Manual.

6.0 EQUIPMENT AND SUPPLIES

6.1 Gas Chromatograph (HP5890 Series I or II or equivalent) analytical system equipped with a packed or split/splitless injection port, 5 meter 0.25mm ID Guard column, 30 meter 0.25mm ID analytical column and flame ionization detector (FID).

6.2 Autosampler (HP2622 or equivalent)

6.2 Data System: A data system capable of recording detector signal, reintegration and quantitation (Multichrom or equivalent).

6.3 Fused Silica Capillary Column: n RTX-5 95% dimethyl -5% diphenyl polysiloxane (30m x 0.25mm ID, 0.25 um) or equivalent.

7.0 REAGENTS AND STANDARDS

7.1 Methylene Chloride - JT Baker, Resi-analyzed, Cat. No. JT9264-03

7.2 Acetone - JT Baker analyzed Ultra-Resi-Analyzed, Cat. No.

7.3 Stock Standard Solutions

Purchase standard solutions pre-made, pre-certified or prepare by accurately measuring a volume of stock standard *(Vstock)*, dissolving the stock standard in solvent and diluting to volume *(Vspike)* in a volumetric flask. The "recipes" on the next page offer guidance for the preparation of standard solutions used for this method.

7.3.1 TPH Surrogate

Stock Standard (Ultra Scientific)	*Cstock (mg/L)*	*Vstock (mL)*	*Vspike (mL)*	*C spike (mg/L)*
o-terphenyl	10,000	1.0	100	100

Solvent: Methylene Chloride

7.3.2 Diesel Calibration Standard Solutions

Stock Standard (Restek)	*Cstock (mg/L)*	*Vstock (mL)*	*Vspike (mL)*	*C spike (mg/L)*
Diesel Level 1	50,000	0.008	4.0	100
Diesel Level 2	50,000	0.016	4.0	200
Diesel Level 3	50,000	0.080	8.0	500
Diesel Level 4	50,000	0.080	4.0	1000
Diesel Level 5	50,000	0.160	4.0	2000
Diesel ICV Standard	50,000	0.040	4.0	500

Solvent: Methylene Chloride

7.3.3 Motor Oil Calibration Standard Solutions

Stock Standard (Restek)	*Cstock (mg/L)*	*Vstock (mL)*	*Vspike (mL)*	*C spike (mg/L)*
Motor Oil Level 1	50,000	0.008	4.0	100
Motor Oil Level 2	50,000	0.040	4.0	500
Motor Oil Level 3	50,000	0.160	8.0	1000
Motor Oil Level 4	50,000	0.160	4.0	2000
Motor Oil Level 5	50,000	0.240	4.0	3000

Solvent: Methylene Chloride

7.3.4 Retention Time Standard

Stock Standard	*Cstock (mg/L)*	*Vstock (mL)*	*Vspike (mL)*	*C spike (mg/L)*
C10	5000	0.020	10	10
C23	5000	0.020	10	10

Solvent: Methylene Chloride

Cstock=Concentration of Stock Standard
Vstock=Volume of Stock Standard Used
Vspike=Volume of Working Standard
Cspike=Theoretical Concentration of prepared Working Standard

7.3.5 All prepared standards must be labeled with the lot number, name, and concentration of the standard along with the expiration date of the standard solution. The expiration date of TPH standards is 6 months from the date or preparation. New standards may and should be prepared more frequently if degradation is evident.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

8.1 Soil, sediment and water samples are collected in amber jars or bottles with Teflon-lined screw caps. Additional requirements for sample collection may be described in site-specific sampling plans.

8.2 Following collection, all samples must be cooled to 4°C (±2°C).

8.3 Soil and sediment samples must be extracted with 14 days of sample collection. Water samples must be extracted within 7 days of collection. All samples must be analyzed within 40 days of extraction.

8.4 Samples and sample extracts are stored separately in temperature controlled storage areas from the time of receipt in the laboratory until a minimum of 30 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or client-specific requirement, samples and sample extracts are disposed of after 30 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

9.1 A method blank and lab control sample (LCS) must be performed with each preparation batch. A matrix spike/matrix spike duplicate is performed at the frequency specified in the client project plan or at a frequency of one MS/MSD per every 20 field samples per site-specific matrix over time. If insufficient sample volume is available to perform the MS/MSD, a lab control sample duplicate (LCSD) must be performed.

9.2 All field samples, QC samples (MB, LCS, LCSD) and the matrix spikes (MS/MSD) are fortified with surrogate standard.

9.3 The LCS, LCSD, and the matrix spikes (MS/MSD) are fortified with spike solution that contain all analytes of interest.

9.4 The criteria that are used to assess quality control samples are provided in Appendix A of this SOP.

10.0 CALIBRATION AND STANDARDIZATION

10.1 GC Operating Conditions:

Initial Temperature	50°C
Initial Time:	4.0 minutes
Ramp Rate 1:	20°C/minute
Temperature 1:	300°C
Ramp Rate 2:	5°C/minute
Final Temperature:	320°C
Final Time:	5.5 minutes
Injection Port Temperature:	290°C
Detector Temperatures:	320°C
Injection Volume:	1 uL
Linear Gas Flow Rate	0.98 uL/min He
FID Make-Up:	20 mL/min.
FID Hydrogen:	20 psi
FID Air:	36 psi

10.2 External Standard Calibration Procedure

10.2.1. Prior to sample analysis, analyze a five-point calibration curve for diesel oil followed immediately by a five-point calibration curve for motor oil.

10.2.2 Prepare the diesel and motor oil calibration standards at a minimum of five concentrations following the procedure described in section 7.3 of this SOP.

10.2.3 Inject each calibration standard and the RT standard into the gas chromatograph using the auto sampler. Using the Multichrom data system, prepare a calibration curve for each analyte and calculate the correlation coefficient. The five-point calibration curve must have a correlation coefficient ≥ 0.995. The RT standard is used to help aid in the identification of target analytes.

10.3 Initial Calibration Verification Check Standard

10.3.1 Prepare the diesel ICV check standard at the mid-level concentration range using the procedure described in section 7.3 of this SOP. The ICV check standard must be prepared from a separate source than the stock standard solutions used for the calibration standards. Inject the ICV check standard into the gas chromatograph using the auto sampler. Using the Multichrom data system, calculate the percent difference using Equation 1 (See Section 12.0), if the %D varies by more than ±15%, then investigate preparation of calibration standards and ICV standard for error, if necessary re-prep calibration standard solutions and repeat initial calibration procedure.

10.4 Continuing Calibration Verification

10.4.1 Verify the working calibration curve after every 10 sample injections or after the instrument has been idle for a time period of more than 8 hours using a mid-level calibration standard that alternates between diesel and motor oil.

10.4.2 Inject the calibration check standard (CCV) into the gas chromatograph using the auto sampler.

10.4.3 Using the Multichrom data system, calculate the percent difference. If the %D varies by more than ±15%, re-analyze the CCV and if repeat failure prepare a new initial calibration curve.

11.0 PROCEDURE

11.1 Transfer an aliquot of each 4 mL extract into an auto-sampler vial with insert.

11.2 Using the Multichrom data system, create the "Edit Run Sequence" to list all laboratory numbers and client identifications for the autosampler rack, and create a new method file to control the data acquisition and post acquisition processing programs. Initiate the "Start Run" program to create the analysis file number where associated data files are stored during acquisition and post acquisition. Once the run sequence set-up is complete and keyed to acquire data, verify the autosampler positions and then start the autosampler sequence.

11.3 Using the Multichrom data system, evaluate the resulting chromatograms. Diesel fuel and motor oil are identified by hydrocarbon pattern matches rather than retention time markers. The diesel fuel pattern generally begins slightly before C8 and the motor oil pattern generally begins after C23.

Integrate samples that do not have chromatographic patterns that match diesel fuel or motor oil to best represent the envelope of hydrocarbons present and quantitate using the best match for diesel fuel or motor oil. The following data qualifiers may be used to help identify the chromatographic pattern if it does not match diesel or motor oil.

Y - A fuel mixture pattern is detected, but the fuel mixture does not fall 90 percent within the calibration standard range and exhibit a reasonable pattern match to any of the calibrated fuels.

Z - Unknown single peaks or chromatographic patterns are detected but do not resemble a typical fuel pattern.

11.5 Review the target analyte concentration for each sample. If the concentration exceeds the linear range of the calibration curve, dilute the extract and reanalyze. The concentration of the diluted extract should be within the upper half of the calibration curve.

12.0 CALCULATIONS

The following equations are used in this method.

12.1 Calculation of Percent Difference

Equation 1: Percent Difference (%D)

$$\%D = \frac{\text{nominal concentration} - \text{calculated concentration}}{\text{nominal concentration}} \times 100$$

12.2 Calculation of Aqueous Sample Concentration

Equation 2: Calculation of Aqueous Sample Concentration

$$\text{Concentration (mg/L)} = \frac{[\text{Extract Concentration} * \text{Extract Volume(L)}] * \text{DF}}{\text{Sample Volume (L)}}$$

Where:
DF= Dilution Factor

12.3 Calculation of Soil/Sediment Sample Concentration

Equation 3: Calculation of Soil/Sediment Sample Concentration

$$\text{Concentration (mg/Kg)} = \frac{[\text{Extract Concentration} * \text{Extract Volume(L)}] * 100 * \text{DF}}{\text{Sample Weight (Kg)} * \%\text{Solids}}$$

Where:
DF= Dilution Factor

13.0 METHOD PERFORMANCE

13.1 The accuracy and precision limits for this method are provided in Table 1 of the Appendix to this SOP.

13.2 Water, Soil and Sediment reporting limits (RL) and method detection limits (MDL) are provided in Table 1 of the Appendix to this SOP.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Whenever feasible, laboratory personnel use pollution prevention techniques to minimize the production of waste in the laboratory.

14.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

15.0 DATA ASSESSMENT, CRITERIA AND CORRECTIVE ACTION

15.1 The criteria used to assess the results for the calibration procedure are provided in Table 2 of the Appendix to this SOP.

16.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

16.1 Data that does not meet the minimum acceptance criteria is flagged using CLP, laboratory or project specific data qualifiers. A complete description of the outage is written in the case narrative provided with the data package report.

16.2 For systematic problems noted, a corrective action report is initiated for investigation and follow-up is performed.

17.0 WASTE MANAGEMENT

17.1 Waste management is performed in accordance with applicable federal, state and local regulations. The laboratory procedure for waste management is described in SOP LP-LB-001HAZWD.

18.0 REFERENCES

18.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

19.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION FORMS

Appendix A

Appendix A: TPH by GC/FID

Table 1: Compound List and Reporting Limits

Compound	MDL *(ug/L)*	MDL *(mg/Kg)*	RL *(ug/L)*	RL *(mg/Kg)*	Accuracy Limits %R	Precision Limit %RPD
Diesel Fuel	0.0472	2.98	0.100	6.67	60-140	≤ 30%
Motor Oil	0.0934	6.07	0.100	6.67	60-140	≤ 30%
MS/MSD	NA	NA	NA	NA	50-150	≤ 30%

(1) The accuracy limits for the MS/MSD are considered advisory.

(2) The RL is adjusted in the final data report to account for dilution factor, percent solid determinations, and sample volume.

Table 2: QC Acceptance Criteria and Corrective Action Matrix

TPH – Diesel and Motor Oil by Method 8015			
Quality Control Criteria	**Frequency**	**Acceptance**	**Corrective Action**
Initial calibration (ICAL)	As Required	Correlation coefficient ≥ 0.995	Recalibrate, mix new standards, reanalyze
Initial Calibration Verification (ICV)	With each ICAL	± 15% quantitation column	Reanalyze, check standard prep, re-prep standards, recalibrate.
Continuing Calibration Standard (CCAL)	Every 10 samples , every 12 hours and after instrument has been idle for more than 8 hours	± 15% quantitation column	Reanalyze check integrations, mix new std. Reanalyze ICAL
Method Blank	Each extraction batch	Targets < ½ RL	Reanalyze, If confirmed, re-extract entire batch.
Samples	--	Concentrations below highest calibration standard	Dilute and reanalyze samples that are more concentrated than the highest calibration standard
Surrogates	Every sample, blank and QC sample must be spiked with surrogate	60-140% Aqueous 60-140% Soil and Sediment	Any sample with outages must be reanalyzed to confirm.
Matrix Spike/Matrix Spike Duplicate	As specified in the client project plan or at a frequency of one MS/MSD per every 20 field samples per site-specific matrix.	50-150% (Advisory) 30% RPD (Advisory) Comparable results for spike and duplicate	Evaluate LCS. If compounds failing in MS/MSD are acceptable in the LCS the outages will assume to be matrix related.
LCS LCSD	LCS= each extraction batch LSCD= when no client MS/MSD is specified	60-140% Aqueous 60-140% Soil and Sediment	Check Std., Check Quantitation, Evaluate MS/MSD. Reanalyze batch if failing compounds are present in the samples.

APPENDIX A-94

STANDARD OPERATING PROCEDURE FOR BULK DENSITY DETERMINATION

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE188_01.DOC
REVISION NUMBER: 01

STANDARD OPERATING PROCEDURE FOR BULK DENSITY DETERMINATION

MAY 26, 2002

COPY #

Property of Northeast Analytical Inc

STANDARD OPERATING PROCEDURE

Author: John Nicpon
Reviewed by:

William Kotas
QA/QC Officer

Approved by:

Robert E. Wagner
Laboratory Director

Northeast Analytical, Inc.
Issuing Section: Inorganics Laboratory
SOP Name: NE188_01.SOP
Date: 5/26/2002
Revision Number: 01

1.0 TITLE

Standard operating procedure for the determination of Bulk Density.

2.0 PURPOSE

To provide the SOP for the preparation and analyses of soil samples for the determination of Bulk Density.

3.0 SCOPE

This method is applicable to soil, peats and soil mixtures. This procedure is based on procedures found in ASTM Method D4531-86 (1996).

4.0 COMMENTS

The difference in the varying bulk density procedures is in the method in which the sample is obtained and the volumes that are used. Variation in bulk density is attributable to the relative proportion and specific gravity of solid organic and inorganic particles and to the porosity of the soil.

5.0 SAFETY

5.1 Safety glasses, lab coat or lab apron and disposable gloves must be worn when handling chemicals and samples.

5.2 Personnel should familiarize themselves with the necessary safety precautions by reading MSDS information covering any chemicals used to perform SOP.

5.3 Samples that emit undesirable odors when heated should be placed in the oven at the end of the day. The oven used for drying samples is connected to a fume hood. The hood should be operational at all times. If the hood is not working properly, contact a member of the safety committee immediately.

5.4 If samples contain known quantities of hazardous material, the dried samples and the drying dishes or cups are classified as hazardous waste and are subject to the procedures listed in SOP NE054.

6.0 REQUIREMENTS

6.1 Knowledge of the operation and calibration of the analytical balance is required.

6.2 Knowledge of the operation of the drying oven located in the Inorganics laboratory.

6.3 Knowledge of the maintenance of the portable desiccator box.

7.0 EQUIPMENT

7.1 Apparatus and Equipment. Located in the Inorganics laboratory.

7.1.1 VWR model 1370FD model drying oven. (A calibrated thermometer is placed in a sand filled bottle inside the oven which is located in the metals laboratory).

7.1.2 Analytical balance. Mettler model AG204. Located in the metals lab.

7.1.3 Aluminum drying dishes. VWR p/n 25433-008. Located in the lab storage room.

7.1.4 Plastic spoons. Located in the inorganics department. Available at local stores.

7.1.5 Bulk Density, % Moisture and % Total Solids logbook. Located in the metals laboratory

7.1.6 Glass trays. Located throughout the laboratory.

7.1.7 Portable desiccator. Located in the metals laboratory.

7.2 Operation of drying oven.

7.2.1 Before drying samples, the drying oven "set temperature" knob has to be adjusted so that the temperature is between 103° and 105° C.

7.2.2 After adjusting the temperature, wait approximately 15 minutes and open the door and read the thermometer. If the temperature is not within the specified range, repeat 6.2.1. If the oven will not stabilize, contact the inorganics manager.

7.3 Calibration of GFAA cups

7.3.1 Calculate the average volume of the GFAA cups annually.

7.3.2 Prepare 10 GFAA cups by numbering them "1" through "10".

7.3.3 Place the cups in a vial rack and place in the drying oven for a minimum of one hour at a temperature of 103° to 105° C.

7.3.4 Each day that the cups are to be weighed, pull the desiccant material from the oven and place in the desiccator for a minimum of one hour before placing the rack and cups in the desiccator. At the end of the day the desiccant material is poured into a glass tray and placed in the drying oven at 103° to 105°C. Place the cups in the desiccator for exactly one hour.

7.3.5 Place a cup on the balance and write the cup number in the logbook. Record the weight of the cup.

7.3.6 Repeat the above process for each cup.

7.3.7 Fill each cup to the top with laboratory grade water.

7.3.8 Carefully record the weight of the cup and water under "WETSAW" column. Subtract the weigh of the cup from the "WETSAW". Record the water weight under the "Comments" column.

7.3.9 Calculate the average water weight and record under the "Comments column".

7.3.10 Divide the average weight of the water in each cup by the density of water (1 g/ml) to calculate the average volume of water in each cup. Record the average volume (ml) under "Comments" column.

7.3.11 Sample cups may be purchased from Perkin Elmer p/n B008-7056 or any other vendor of 2ml GFAA cups.

8.0 PROCEDURE

8.1 Sample Analysis.

8.1.1 Prepare the GFAA sample cups by writing the last three digits of the NEA sample ID on the cups, for example, the sample cup for NEA sample AB01234 would be labeled as '234'. Prepare extra sample cups with their own unique numbers.

8.1.2 Place the cups in a vial rack and place in the drying oven for a minimum of one hour at a temperature of 103° to 105°C.

8.1.3 Each day that the cups are to be weighed, pull the desiccant material from the oven and place in the desiccator for a minimum of one hour before placing the rack and cups in the desiccator. At the end of the day the desiccant material is poured into a glass tray and placed in the drying oven at 103° to 105°C. Place the cups in the desiccator for exactly one hour.

8.1.4 Set up the logbook by writing the NEA#'s under the appropriate column.

8.1.5 Access LIMs and go to 'WIN RESUTS'. Select "SAMPLE DESIGNATION" and type the NEA#'s in the white box. Select the 'TEST' template and click 'OK'.

8.1.6 Place a cup on the balance and write the cup number in the logbook. See the following table to determine what column heading and cell to use.

8.1.7 Right click and select "Take BOAT". Copy the value from the cell into the logbook. Repeat process for all the samples.

8.1.8 Using a tongue depressor or spatula, carefully place a portion of well mixed sample into the cup (do not use rocks or stones). Remove air pockets in the cup by gently tapping the cup on the counter. Fill the cups to the top.

8.1.9 Access LIMs and go to 'WIN RESULTS'. Select "SAMPLE DESIGNATION" and type the NEA#'s in the white box. Select the "TEST" template and click "OK".

8.1.10 Place each cup on the balance. Right click and select "Take "WETSAW". Copy the value from the cell into the logbook. Repeat process for all the samples.

8.1.11 Place the cups in a vial rack and place in the drying oven OVERNIGHT at a temperature of 103° to 105°C.

8.1.12 Place the cups in the desiccator for exactly one hour.

8.1.13 Access LIMs and go to "WIN RESULTS". Select "SAMPLE DESIGNATION" and type the NEA#'s in the white box. Select the "TEST" template and click "OK".

8.1.14 Place a cup on the balance. See the following table to determine what column heading and cell to use.

8.1.15 Right click and select "Take DRYSAW". Copy the value from the cell into the logbook. Repeat process for all samples.

8.1.16 Enter the average volume of the cups under "BDMCVO".

8.1.17 The results are automatically calculated.

9.0 SAMPLE COLLECTION AND STORAGE

9.1 No preservation is required.

9.2 Samples can be collected in plastic or glass bottles with Polyseal caps.

10.0 QUALITY CONTROL

10.1 Duplicates:

10.1.1 One duplicate sample is processed each day that samples are prepared or every 10 samples, which ever occurs first.

10.2 Criteria:

10.2.1 % RPD = ABS[(X1-X2)/(X1+X2)]*200.

10.3 Limits:

10.3.1 The % RPD must be less than 20 %. If not samples need to be reanalyzed.

11.0 DOCUMENTATION

11.1 In the logbook, record the temperature of the oven and the date and time that the sample cups were placed in the oven.

11.2 In the logbook, record the temperature of the oven and the date and time that the sample cups were taken out of the oven.

11.3 Copies of the LIMs sheets are to be reviewed against the logbook by the analyst and placed in the folder.

11.4 LIMS Result Entry Template:

LIMS RESULT TEMPLATE "TES T" COLUMN HEADINGS AND DESCRIPTIONS

Column	Description	Column	Description	Column	Description
%SOLIDS	Percent solids	**BOATWT**	Cup or boat wt.	**WETSAW**	Cup and wet sample wt.
BULK	Bulk density	**BDMCVO**	Cup volume ml.	**MOIST**	% Moisture
D_BULK	Dup. Bulk density	**BDMCDVOL**	Cup volume ml.	**DUPBOATWT**	Dup. boat wt.
P_BULK	Precision calculation	**D_MOIST**	Dup. %Moist.	**WETDUPWT**	Dup. wet sample wt.
P_MOIST	Precision calculation	**DRYDUPWT**	Dup. dry sample wt.	**DRYSAW**	Dry sample wt.

12.0 POLLUTION PREVENTION/WASTE MANAGEMENT.

12.1 Refer to NEA168.SOP for instructions for pollution prevention.

12.2 Refer to NEA089.SOP and NEA054.SOP for instructions for disposal of waste generated during the procedures previously mentioned.

13.0 DEFINITIONS

13.1 Analytical Batch – The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples that are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g. groundwater, sludge, ash, etc.)

13.2 Bulk Density – Is the measure of the weight of the soil per unit volume (g/ml), usually given on an oven dry (110° C) basis.

13.3 Matrix – The predominant material of which the sample to be analyzed is composed.

13.4 MSDS – Material safety data sheet. OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs. The thrust of the law is to have those who make, distribute, and use hazardous materials responsible for effective communication.

13.5 Relative Percent Difference (RPD) – To compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

13.6 Replicate – Repeated operation occurring within an analytical procedure. Two or more analyses for the same constituent in an extract of a single sample constitute replicate extract analyses.

13.7 RCRA – Resource Conservation and Recovery Act, PL 94-580. Found at 40 CFR 240-271. EPA has jurisdiction. Enacted November 21, 1976, and amended since. RCRA's major emphasis is the control of hazardous waste disposal. It controls all soil-waste disposal and encourages recycling and alternative energy sources.

13.8 RCRA Hazardous Waste – A material designated by RCRA as hazardous waste and assigned a number to be used in record keeping and reporting compliance.

13.9 Reagent Water – Water in which interference is not observed at or above the minimum quantitation limit of the parameters of interest.

13.10 Rounding Rules – If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by

13.10.1 If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number.

13.10.2 If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.

13.11 Sample Delivery Group (SDG) – Unit within a single case that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer field samples within a case, received over a period of up to 14 calendar days (7 calendar days for 14-day data turnaround contracts). Data from all samples in an SDG are due concurrently.

14.0 REFERENCES

14.1 ASTM methods D4531-86 (1996).

APPENDIX A-95

STANDARD OPERATING PROCEDURE: CHLOROPHYLL-A DETERMINATION

STANDARD OPERATING PROCEDURE:

CHLOROPHYLL -a DETERMINATION

OBTAINED FROM:

AQUATEC BIOLOGICAL SCIENCE
75 GREEN MOUNTAIN DRIVE
S. BURLINGTON, VT 05403

8.0 CHLOROPHYLL *a*

8.1 Introduction

The concentration of photosynthetic pigments is used to estimate phytoplankton biomass. All green plants contain chlorophyll *a* and this constitutes 1 to 2% of the dry weight of planktonic algae. Other pigments, such as chlorophyll b and c, as well as chlorophyll degradation products, such as phaeophytins are also found in aquatic environments.

Chlorophyll *a* can be determined by spectrophotometric, fluormetric and high performance liquid chromatographic techniques. The method here employs fluorometry, which is more sensitive than spectrophotometry and utilizes less sample. One drawback, however, is that two common degradation products of chlorophyl *a* and pheophytin *a* can interfere with the chlorophyll *a* determination. These pheopigments can be measured, but are unreliable if chlorophyll *b* is present. Upon acidification of chlorophyll *b*, the resulting fluorescence emission of pheophytion *b* is coincident with that of pheophytin *a*, producing an underestimation of chlorophyll *a* and an overestimation of pheopigments.

In the handling of samples for chlorophyll a samples, the biggest causes of chlorophyll degradation are light, temperature, and acidity.

8.2 Sample Handling

- 100 ml to 200 ml of sample is usually sufficient for chlorophyll *a* analyses.
- Samples should be put in clean glass or plastic containers. If container is not opaque the container should be wrapped in foil.
- Samples should be kept cold (1-4 °C), not frozen, and in the dark from collection time onward.
- If samples are field filtered, following Section 8.3 below, freeze the filters and keep frozen until they have been analyzed.
- Samples should be logged in by sample management in subdued light and transported to microbiology in a cooler as soon as possible after receipt.

8.3 Sample Filtration

8.3.1 Equipment and Reagents

- 100 ml graduated cylinder
- Fiber filters Whatman glass (GF/B) or Gelman (AE)

- Glass filtering apparatus
- Saturated magnesium carbonate solution
- Forceps
- Opaque (black) petri dishes
- Vacuum pump

8.3.2 Laboratory Procedure

- Set up filtering apparatus. Set vacuum on pump to <100 mm Hg.
- Handle filters with designated forceps only, and do not touch the inside of any glassware.
- Carry out the procedure in subdued light.
- Shake sample thoroughly.
- Using the specially prepared graduated cylinder, measure a 100 ml aliquot of sample. Sample volume may vary according to turbidity and algae concentration.
- Record the volume filtered on form.
- After adding the 100 mls of sample into the filtering flask, add 1 ml of saturated magnesium carbonate. Filter sample with 100 mm Hg or less of vacuum. Rinse vessel once with 5 ml deionized water.
- After filtration, remove the filtering funnel and fold the filter in half, using the forceps. Transfer the filter to an opaque (black) petri dish and label each petri dish with sample ID number.
- Rinse the filtering vessel and graduated cylinder twice with deionized water prior to filtering the next sample.
- For each BTR or twenty samples filtered, a reagent blank should be prepared by filtering DI water through a glass fiber filter and processing it as if it were a sample. The volume value for the control is entered as 1.
- When all samples are filtered: 1) rinse all filtering funnel parts and the graduated cylinder with DI water before storing. 2) wrap the perti dishes in batches of eight with aluminum foil. Label with parameter, date, client, and sample numbers. 3) store in freezer in sample management. Filters should be stored in the freezer at least overnight but not more than 21 days. Additional storage time can result in some decrease in chlorphyll a concentration. In addition, if the whole water pH is less than 5, then the extraction process should be initiated as soon as possible. 4)

include date, time, and initials on the chlorophyll *a* analyses worksheet. Fill in the correct information.

8.4 Pigment Extraction

8.4.1 Equipment and Reagents

- Tissue grinder (1/4" drill)
- Glass grinding tube with matching pestle with TFE tip.
- Centrifuge
- 15 ml centrifuge tubes plus caps
- saturated magnesium carbonate
- 90% buffered acetone solution

8.4.2 Laboratory Procedure

- Be sure to turn on the ventilation fan before working with the acetone.
- Allow filters to thaw. Be sure room lighting is subdued before opening.
- Using the designated forceps, insert the filter into the grinding tube. Add 5-10 ml of aqueous acetone.
- With the pestle in the drill bit macerate the filter, at 500 rpm for 1 min. The sample should be well ground.
- Transfer sample to a screw cap centrifuge tube.
- Rinse grinder with 90% aqueous acetone and add to the centrifuge tube. Cap tube.
- Steep sample at least 2 hours, but not more than 24 hours, at 4 °C in the dark.
- Wrap centrifuge tubes in foil during storage.
- Remove the tubes from the refrigerator and allow to warm to room temperature in the dark.
- Mix the tube by inverting and centrifuge at 500 g (2500 rpm) for twenty minutes.
- Decant the clarified extract into a 25 or 50 ml volumetric flask and dilute to volume with 90% aqueous acetone. Stopper the volumetric flask and mix by inversion at least twelve times. This volume is the extract volume and should be entered as such on the chlorophyll *a* worksheet.

8.5 Fluorometric Determination of Chlorophyll *a*

8.5.1 Equipment and Reagents

- Turner design model TD-700 fluorometer equipped with 10-045 Daylight White lamp, photomultiplier tube (red-sensitive), and excitation (10-050R) and emission filters (10-051R) .
- Fluorometer cuvette
- Volumetric flasks
- Glass pipettes
- 1 NHCl
- Aqueous 90% acetone with $MgC0_3$ (for samples)

8.5.2 Laboratory Procedure

8.5.2.1 Fluorometer Calibration

The TD-700 is calibrated and operated in the Multi-Optional Mode - Direct Concentration mode. In this mode the TD-700 will display the actual concentration in the selected units. The calibration procedure for the Multi-Optional Mode is as follows:

- ➢ Press <ENT> from the HOME screen, then press <1> for Setup, then <1> again for Mode. Use <ϕ> to choose the Multi-Optional Mode. Next press <ESC> to return to the previous screen, then press <2> to choose the calibration procedure. Use the <ϕ> key to choose "Direct Conc" for the Direct Concentration calibration procedure. Next press <ESC> to return to the previous screen, then press <3> to choose the units of measure. Press <ESC> twice to return to the Setup/Cal screen.

- ➢ To begin the calibration sequence press <2> from the Cal/Setup screen; the Direct Concentration calibration sequence will appear. When prompted to enter the maximum range (the maximum concentration to be read), press <1> to accept the current value or <9> to enter a new value. The range of acceptable values is 1-1000.

- ➢ Next enter the number of standards that will be used to calibrate the TD-700 (1-5 concentrations. It is recommended that a minimum of 3 standards be used.

- ➢ When the TD-700 calls for the "HiStd Conc", press <1> to accept the current value and advance to the next screen. Press <9> to change the value. Enter the actual concentration of the highest concentration standard (Hi Std) to be used and press <ENT>. The Hi Std should be about 80% of the Max range previously selected. The acceptable range for all standards is 0.1 to 1000. The concentrations of the standards selected must be within the max range previously selected and the difference in concentration between any two standards should not be less than 10% of the max range selected. Calibrate using the highest concentration first then use standards 2-5 in any order.

- Fill a clean 13 x 100 mm cuvette with the Hi Std. Wipe the outside of the cuvette dry and insert it into the sample adaptor in the sample chamber and close the lid. Press <*>. The TD-700 will adjust the sensitivity (as shown by the SENS FACTOR) to the level appropriate for that standard then read the standard.

- The TD-700 will prompt you to enter the actual concentration of the second standard (#2 Std) and to insert the second standard, then the third (#3 Std), etc. Use a clean, rinsed cuvette and insert the next standard; press <*>; then <ENT> when finished.

- When all standards have been run, the TD-700 will prompt you to insert the Blank. Fill a clean cuvette with the Blank (90% acetone solution), wipe the outside dry, and insert it into the sample adaptor in the sample chamber. Press <ENT>.

- Wait for the Blank reading to stabilize, the press <0>. The TD-700 will read the Blank, then automatically return to the HOME screen. Calibration data will printout automatically to the laptop computer.

- This calibration procedure must be performed whenever the lamp, or filters are replaced or if the measured concentration of the solid standards differs from the value established during the most recent calibration event by more than 10 percent. The TD-700 must be calibrated at least annually.

- Calculate the "r" factor during calibration by measuring the concentration of a primary standard prior to (R_b) and after (R_a) acidification. Acidify 5 ml of the primary standard by adding 0.15 ml of 0.1 N HCl (3 drops), mix, wait 90 seconds, then record the chlorophyll *a* concentration. Calculate r as follows:

$$r = R_b/R_a$$

8.5.3 Flurometric Standards

- Turner Designs Solid Secondary Chlorophyll *a* standards are calibrated against the liquid primary chlorophyll *a* standards in acetone (the concentration of the primary standards are determined spectrophotometrically by Turner Designs).

- Results should be ± 10% of the calculated value.

- At least one standard is measured per run or with every twenty samples.

8.5.4 Determination of Chlorophyll *a* in Sample

- Insert the appropriate excitation (10-050R) and emission filter (10-051R) as per manufacturer's instructions. Turn on the TD-700 and allow it to warm up for 10 minutes. Make certain the lamp (10-045 Daylight White lamp) is functioning.

- From the final extract derived from the extraction procedure in 8.4.2 above the chlorophyll *a* and pheophytin *a* can be determined on a calibrated fluorometer. Add approximately 5 ml of sample to a clean 13 x 100 mm glass cuvette.

- Measure sample fluorescence by placing the cuvette into the sample chamber, close the chamber, then press <*>. The chlorophyll *a* concentration is automatically sent to the computer, however the concentration should also be manually recorded on the chlorophyll *a* analysis benchsheet. This is the R_d value (uncorrected for pheophytin *a* content).

- Remove the cuvette from the fluorometer and acidify the sample by adding 0.15 ml of 0.1 N HCl (3 drops). Shake tube gently to mix the acid and sample.

- Place the cuvette back into the fluorometer, wait 90 seconds, then read and record the chlorophyll *a* concentration. This is the R_c value for the sample.

- Record the R_d and R_c values for each sample. The chlorophyll *a* and pheophytin *a* concentrations are calculated as follows:

$$\text{Chlorophyll } a\text{, } \mu g/L = (r/r - 1)(R_d - R_c)$$

$$\text{Pheophytin } a\text{, } \mu g/L = (r/r - 1)(rR_c - R_d)$$

where;

r = the before:after ratio of a pure chlorophyll *a* solution
R_d = concentration of a sample extract before acidification
R_c = concentration of a sample extract after acidification

The concentration of chlorophyll *a* and pheophytin *a* in the original sample is calculated by multiplying the results of the above equations by the extraction volume (in milliliters) and dividing by the volume (in milliliters) of sample filtered. Any dilution or concentration factors must also be incorporated accordingly.

- After the sample has been analyzed, pour the acetone extract into a labeled "waste" container to be disposed as "solvent waste" in the Hazardous Waste Room.

- Fill in date, initials, and all other appropriate information on the chlorophyll *a* worksheet.

8.6 Quality Control

A method blank, a blank filter carried through the entire process, is created at the beginning of each run. In addition, a solid secondary chlorophyll *a* standard will be measured at the beginning of each run and after every twenty samples. The measured value should be ± 10% of the standards calculated value. The reporting limit is <0.1 µg/L.

8.7 Cleaning Glassware

It is important that glassware be clean and acid free.

Materials:

Liquinox
$NaHC0_3$
$NaHC0_3$ buffered acetone

8.7.1 Laboratory Procedure

- Wash the glassware in liquinox and water, using the brushes reserved for washing chlorophyll glassware.
- Rinse the glassware thoroughly in tapwater. If the glassware has been in contact with acid, rinse with $NaHC0_3$ solution 2-3 times.
- Rinse again thoroughly with tapwater.
- Rinse once with DI water.
- Triple rinse with 90% $MgC0_3$ buffered acetone.
- Air or oven dry.

8.8 Reagents for Chlorophyll *a* Analysis

8.8.1 Saturated Magnesium Carbonate Solution

Dissolve 1 g $MgC0_3$ in 100 ml DI water or 10 g of $MgC0_3$ in 1 liter of deionized water. Mix thoroughly and allow to settle. Use supernatant to prepare 90% buffered acetone.

8.8.2 Sodium Bicarbonate Solution (1N)

Weigh 8.4g $NaHC0_3$ into a 100 ml flask and dilute to volume with DI water. Mix well before use.

8.8.3 90% Buffered Acetone

For grinding of filters and dilutions of chlorophyll *a* extraction.

Mix 900 parts acetone with 100 parts saturated magnesium carbonate solution. 900 ml acetone plus 100 ml of magnesium carbonate solution will not equal 1L.

8.8.4 1N HCl

Pipette 8.4 ml concentrated HCl into a 100 ml flask. Dilute to volume with DI water an mix well before use.

8.8.5 Sodium Bicarbonate Solution

For rinsing glassware. Dissolve 8.4 g $NaHC0_3$ in 1 L of DI water. Mix well.

8.9 Data Reduction

Using Excel 97, import the TD-700 data text file and calculate the chlorophyll *a* and pheophytin *a* concentrations for each sample. When complete, print the Excel worksheet and attach it to the BTR worksheet.

8.10 Laboratory Transcription

Record corrected, uncorrected and pheophytin *a* values (if requested) on the appropriate BTR worksheets. Be sure to include the units as µg/L. All calculations and transcriptions are QC'd by another laboratory technician, who will sign and date the laboratory analysis worksheet.

8.11 Reporting Results

Enter the concentration data for each sample into the LIMS "Results Entry Form"; when complete, submit all worksheets and reports to the Quality Assurance Officer or other designated person for review. Results will be checked, transcribed and reported according to ABS'S standard operating procedure. BTR's and worksheets will be filed according to ABS'S standard operating procedure.

Reference: Standard Methods for the Examination of Water and Wastewater. 19th ed., 1995. "Instructions for Fluorometric Analyses of Chlorophyll *a*." U.S. EPA, 1992.

APPENDIX A-96

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF TOTAL AND PARTICULATE ORGANIC CARBON

STANDARD OPERATING PROCEDURE

Author: Chris Hynes
Reviewed by:

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Approved by:

____

Northeast Analytical, Inc.
Issuing section: Inorganics Department
NE128_03.SOP
Date: 10-February-2000
Revision Number: 3

1.0 TITLE

Standard operating procedure for the determination of total and particulate organic carbon according to Tekmar-Dohrmann application note TOC-011.

2.0 PURPOSE

The purpose of this SOP is to provide procedures for particulate organic carbon (POC) and total organic carbon (TOC).

3.0 SCOPE

This method is applicable to waste water and ground water for POC and TOC, and sediments and filters for TOC.

4.0 COMMENTS

Organic carbon is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample.

The fractions of total carbon (TC) are defined as:
1) inorganic carbon (IC)-the carbonate, bicarbonate, and dissolved CO_2;
2) total organic carbon (TOC)-all carbon atoms covalently bonded in organic molecules;
3) dissolved organic carbon (DOC)-the fraction of TOC that passes through a 0.45-µm -pore-diameter filter,
4) particulate organic carbon (POC)-also referred to as non dissolved organic carbon, the fraction of TOC retained by a 0.45-µm filter.

IC interference can be eliminated by acidifying samples to pH 2 or less to convert IC species to CO_2. Subsequently, purging the sample with a purified gas removes the CO_2.

Principle: Depending upon the configuration, TOC can be measured by ultra-violet promoted persulfate oxidation or high-temperature combustion, followed by infrared detection.

1) TOC and POC in solid and sludge can be measured by utilizing the combustion-infrared method. The sample is homogenized and treated with acid and then heated to remove IC. The treated sample is placed into a heated reaction chamber packed with an oxidative catalyst such as cobalt oxide. The organic carbon is oxidized to CO_2

and H_2O. The sludge and sediment sampler combusts samples at 800°C in an oxygen atmosphere so that solids as well as liquids can be analyzed.
The sampler consists of a magnetically coupled boat inlet system which delivers the sample to the high temperature furnace. Two ports are provided for sample introduction, a septum port for liquid injections, and a flip-top port for solid samples. The CO_2 from the oxidation of organic carbon is transported in the carrier-gas stream and is measured by means of a nondispersive infrared analyzer (NDIR).

2) TOC in aqueous samples can be measured by UV promoted persulfate infrared method. External sparging is used to remove inorganic carbon. The acidified persulfate reagent is continuously pumped from the external reservoir to the injection port and then into the bottom of the UV reactor. The reactor is a constant volume design; the excess liquid is pumped to waste from the drain port. The reactor liquid is continuously sparged and this sparge/carrier gas flows out at the top of the reactor to the NDIR. When a sample containing combined carbon is injected, it is carried into the reactor by the reagent flow. The oxidation of organics occurs rapidly, and the resultant carbon dioxide is sparged from the liquid and carried to the NDIR.

The detection limit for samples is dependent on the amount of sample analyzed.

Note: If the determination of TOC, TC and IC is required for a water sample, an unfixed portion of the sample must be supplied and analyzed for TC. The inorganic carbon fraction of the sample is removed from an aliquot of the preserved sample which is then analyzed for TOC. The IC fraction of the sample is determined by taking the difference between the TOC and TC values.

Sampling and storage: The holding time for analyzing soil samples for TOC is 14 days from the date that the samples are collected. Samples are to be stored at 4°C until the time of analysis.

The holding time for analyzing water samples for TOC is 28 days from the date that the sample was collected. Collect samples in 40 ml VOA vials with silicone rubber-backed TFE septa with open ring caps. Preserve the samples with 1+1 H_2SO_4 or 1+1 H_3PO_4. Samples are to be stored at 4°C until the time of analysis.

The holding time for analyzing water samples for POC is 14 days from the date that the sample was collected. Collect samples in one liter containers with Polyseal caps. Do not add any preservative to the bottles or samples. Samples are to be stored at 4°C until the time of analysis.

5.0 SAFETY

5.1 Safety glasses and disposable gloves must be worn when handling chemicals and samples.

5.2 Personnel should familiarize themselves with the necessary safety precautions by reading MSDS information covering any chemicals used to perform SOP.

5.3 Ultra-violet radiation can cause damage to the eyes. Do not open the door to the UV persulfate module without turning the lamp off.

6.0 REQUIREMENTS

6.1 Method detection limit study.

6.1.1 Seven MDLs samples (spike seven aliquots of laboratory water with the TOC standard) should be determined annually at a concentration of two to three times the estimated instrument detection limit for the analytes of interest.

Analyze the samples according to the procedures set forth in this document. Calculate the MDL by multiplying the standard deviation of seven MDL measurements by 3.14. For the MDL to be valid, it must be greater than 1/10 the amount spiked but not greater than the amount spiked.

6.1.2 Knowledge on the operation and maintenance of the Dohrmann DC-80 series IR-I NDIR detector, UV-persulfate Reaction and sludge/sediment sampler modules.

6.1.3 Trainees are required to read the Instrument manual and take notes on subject matter not covered in SOP. Information about maintenance and replacement on specific parts not covered in SOP should be recorded on the "Notes" page of the SOP for future reference.

7.0 EQUIPMENT

7.1 Equipment.

7.1.1 Dohrmann IR-I NDIR detector module. Located in the main laboratory.

7.1.2 Dohrmann sludge/sediment sampler. Dohrmann (p/n 832-222). Located in the main laboratory.

7.1.3 250 and 1000 µL Rainin autopipets. Rainin (p/n EP-250 and EP-1000).

7.1.4 250 and 1000 µL pipet tips. Rainin (p/n RT-96 and RT-200).

7.1.5 1-5 ml Finn digital pipette with pipet tips. Baxter (p/n P5055-14).

7.1.6 Quartz boats. Dohrmann (p/n 899-624). Located in the main laboratory.

7.1.7 Quartz wool. Dohrmann (p/n 511-735). Located in the main laboratory.

7.1.8 GC oven. Set at 75 ^{o}C. Located in the main laboratory.

7.1.9 Propane tank with torch assembly. Located in the main laboratory.

7.1.10 Tweezers and steel spatula. Located in the main laboratory.

7.1.11 Analytical balance. Located in the main laboratory.

7.1.12 Centrifuge. Located in the main laboratory.

7.1.13 40 ml VOA vials. Located in the bottle storage room.

7.1.14 50, 100 and 250 µl syringe. Located in the main laboratory.

7.1.15 High purity oxygen tank with regulator. Located in the main laboratory.

7.1.16 Aluminum weighing boats. Located in the main laboratory.

7.1.17 Gray septum. Dohrmann (p/n 517-807). Located in the main laboratory.

7.1.18 Pasteur Pipets. Located in all laboratories.

7.1.19 UV-Persulfate Reaction Module. Located in the main laboratory.

7.1.20 Blue injection septum. Dohrmann (p/n 517-811). Located in the main laboratory.

7.1.21 Teflon sleeve reactor, taper joint. Dohrmann (p/n 070-627). Located in the main laboratory.

7.1.22 Lamp, Ultra-violet. Dohrmann (p/n 512-092). Located in the main laboratory.

7.1.23 Peristaltic pump tubing.
  a) PVC Black/Black (p/n 899-641).
  b) PVC Green/Green (p/n 899-645).
  c) Viton A Purple/Purple (p/n 899-651).

7.1.24 High purity nitrogen tank with regulator. Attach plastic tubing to the regulator. Located in the main laboratory.

7.1.25 20-mesh tin. Dohrmann (p/n 511-876). Located in the main laboratory and used for tin/copper scrubber.

7.1.26 Copper. Dohrmann (p/n 511-895). Located in the main laboratory and used for tin/copper scrubber.

7.1.27 Pyrex wool. Dohrmann (p/n 511-895). Located in the main laboratory and used for tin/copper scrubber.

7.2 Reagents.

7.2.1 Laboratory grade water. Located in the cooler room.

7.2.2 ~2500 mg/L TOC stock standard. Mallinkrodt (p/n 6704-1). Dry potassium hydrogen phthalate crystals (primary standard grade) in 104 °C oven for 2 hours and weigh out approximately 2.65675 grams. Record the weight in the Inorganic standard logbook and dissolve in approximately 400 ml of laboratory grade water, add 2 ml of phosphoric acid and bring to a final volume of 500 ml. Calculate the exact concentration of the solution:
(weight of potassium hydrogen phthalate) X 941 = TOC stock standard {mg/L}

7.2.3 TOCS and POC calibration standards:
Prepare 4 calibration standards of different concentrations ranging from ~120.7 - ~1207 mg/L. Record the date and information related to the preparation of the calibration standards in the Inorganic standard logbook.

7.2.4 TOC in water calibration standards (low level):
Prepare 5 calibration standards of different concentrations ranging from ~1.2 - ~24.10 mg/L. Record the date and information related to the preparation of the calibration standards in the Inorganic standard logbook.

7.2.5 7.9N (1+1) nitric acid. Dilute 50 ml of concentrated nitric acid to a final volume of 100 ml. Located in the Inorganics laboratory.

7.2.6 ICV/CCV: TOCS and POC 1000 mg/L TOC control. Ricca (p/n 1847-16). Located in the Inorganics laboratory.

7.2.7 ICV/CCV: TOC in water 10 mg/L TOC control. Ricca (p/n 1847-16). Dilute 1000 mg/L ICV/CCV standard 100x. Located in the Inorganics laboratory.

7.2.8 Concentrated phosphoric acid (H_3PO_4). J.T. Baker. 'Baker analyzed', (Baxter p/n 0260-01*BC). Located in the Inorganics laboratory.

7.2.9 2.0 % potassium persulfate. Add approximately 700 ml of laboratory water to a one liter volumetric flask and add 20 grams of $K_2S_2O_8$ (J.T. Baker 'Baker Instra-analyzed' (Baxter p/n 3239-01*BC)) to the flask with a stir-bar. Add 1 ml of concentrated phosphoric acid to the flask and stir until the $K_2S_2O_8$ has dissolved. Remove the stir-bar and bring to volume.

7.3 Glassware and apparatus.

7.3.1 10, 25, 50, 100 ml Class A volumetric flasks. Located in the Inorganics laboratory.

7.3.2 100 ml graduated cylinder. Located in the Inorganics laboratory.

7.3.3 Rinse bottle. Filled with laboratory grade water. Located in the Inorganics laboratory.

7.3.4 TOC logbook. Located next to TOC instrument.

8.0 PROCEDURE

8.1 Operation and maintenance of the Dohrmann IR-I NDIR detector module.

8.1.1 Refer to the instrument manual for specific instructions and part numbers for all components.

8.1.2 To prepare the tin/copper scrubber, fit one end of the Pyrex scrubber tube with a cored gray septum. Insert a tuft of Pyrex wool and then about 2 inches of tin in the other end. Secure the tin with another tuft of Pyrex wool. Then, fill the remaining half of the scrubber tube with an equal amount of copper. Secure the copper with a third tuft of Pyrex wool. Insert a cored gray septum. Inspect the tin/copper scrubber and change the contents of the tube when one-half of the tin is discolored.

8.1.3 The detector must be on for several hours in order to achieve equilibrium. It is recommended that the detector is turned on the day before the analysis is to be performed. Power up the detector and the main unit.

8.1.4 Verify that the printer has sufficient amount of paper before starting the analysis. Reset the printer so that the number "1" will be printed for the first analysis performed for that day.

8.1.5 Select the "TOC" and the "DET" positions. For the detector, select position "3" for high concentrations, "2" for medium concentrations, and "1" for low concentrations of TOC.

8.1.6 The module will not light the green "ready" light if the baseline is above 0.05. Adjust the "zero" control until the baseline is less than 0.02. The "CALIB" light must be off during analysis.

8.2 Operation and maintenance of the Dohrmann sludge/sediment sampler.

8.2.1 Refer to the instrument manual for specific instructions and part numbers for all components.

8.2.2 A portion of sample is weighed into a quartz boat where it is acidified and dried. The boat is placed in the boat carriage of the sampler and it is moved into the combustion chamber. Gas from the combustion tube flows into the flask to the right where it passes through acidified water.
The gas travels to the flask to the left where excess water is removed before traveling to the detector module. The gas passes through the tin and copper scrubber and into the detector.

8.2.3 Before turning on the solid sampler, carefully examine individual components for sign of wear. Adjust the flow of oxygen to 30 psi. The level of acidified water in the right flask must be above the fritted sparging finger. A vigorous flow of gas emitting from the sparging finger should be easily observed, if not, check the gas lines and connections for leaks. The water collection flask should be emptied on a daily basis.

8.2.4 Turn on the furnace unit. When using the module for the first time or after a long period of inactivity, the furnace should be monitored with a voltmeter to verify that the temperature is at 800°C. Place the black (ground) probe in the "com" port. Place the red (positive) probe in the "monitor", set the voltmeter to "volts". The voltage reading should read "0.80", if not, place the red probe in the "adj" port. The voltage reading should read "0.80", if not, adjust the voltage by turning the set screw until the correct voltage is achieved.

8.2.5 If the gray septum (p/n 517-807) at either end of the combustion tube have corroded and require replacement, the furnace must be turned off before replacing the septum.

8.3 Calibration of Dohrmann sludge/sediment sampler and IR-I NDIR detector module.

8.3.1 Determine the approximate concentration of the samples by analyzing one sample in each of the detector modes. Select the mode where the sample area readout is closest to the middle of the scale.

8.3.2 A new calibration curve must be generated if either the ICV or CCV (see **8.11 Quality Control**) are unacceptable. The calibration curve is based on 'μg of carbon' versus 'area'. Different volumes of the stock standard are injected onto a quartz boat that is lined with quartz wool. The calibration standards require duplicate injections.

8.3.3 A fresh tuft of quartz wool must be inserted into the boat before calibrating the instrument. The boat is placed inside the sediment sampler module. Hook the loop of the boat with the end of the magnetic boat carriage.

8.3.4 Remove contaminates from the boat by placing it in the furnace until the baseline has started to decrease. Pull the boat out of the furnace.

8.3.5 After the boat has cooled (approximately 30 seconds), place the boat underneath the injection port. Remove septum and inject calibration standard onto the boat. Replace septum.

8.3.6 After the baseline has stabilized, place the boat in the furnace. Press the "Start" button. After the signal has started to decrease, pull the boat out of the furnace.

8.3.7 Repeat injection of the standard until consecutive measurements are obtained that are reproducible to within ± 10%.

8.3.8 Repeat **8.3.5-.7** for the remaining calibration standards.

8.3.9 The calibration and continuing check blank consists of 50 ml of laboratory water and one ml of 1+1 nitric acid. Inject 70 µl of the blank solution for the calibration and continuing check blanks.

8.3.10 For TOC solids and POC, inject 70 µl of each calibration standard and the stock standard. If the needle in the IR meter goes past '95' or if the red error light has lit after injecting the stock standard, inject a smaller volume of the standard. Every standard must be within the scale of the detector.

8.3.11 Enter the injection number, standard label, date analyzed, injection volume, and the area printed by the printer in the TOC logbook. See the **Glossary** for information about the correlation coefficient.

8.4 Preparation of solid samples.

8.4.1 Between 1.0 and 20 mg of material can placed in a boat depending on the percent of carbon in the sample. Solid samples are analyzed in duplicate.

8.4.2 The concentration of the samples must be within the range of the calibration curve. If the sample concentration of the sample is outside the range of the calibration curve, repeat the analysis of the sample. If the µg of carbon of the sample was too low, use more sample up to 20 mg. If the sample concentration was too high, use less sample down to 1.0 mg.

8.4.3 Place each boat in a numbered aluminum weigh boat.

8.4.4 Homogenize a portion of the sample.

8.4.5 Place one boat on the analytical balance and tare the balance. Transfer an aliquot of the sample to the boat and record the NEA #, weight and the boat number in the TOC logbook. Place the boat in the numbered aluminum weigh boat.

8.4.6 Repeat **8.4.5** for the replicate sample analysis.

8.4.7 Add 2 to 3 drops of 1+1 nitric acid to each sample. Turn off the GC oven. Place the aluminum weigh boats in the GC oven. Place a 60 ml beaker over each quartz boat. Turn on the GC oven. Remove samples when dried (minimum of 10 minutes).

8.4.8 Place the boat in the raceway. After the baseline has stabilized, place the boat in the furnace and press the 'Start' button.

8.4.9 Copy the TOC area from the printer into the TOC logbook.

8.4.10 After each sample analysis, scrape any remaining material from the boat and place the boat in the flame of the propane torch to remove any contaminates.

8.4.11 Repeat **8.4.3-.9** for the remaining samples.

8.5 Percent total solids determination

8.5.1 Determine the percent total solids for each sample as described in NE090.

8.6 The determination of Particulate organic carbon (POC)in water.

8.6.1 The purpose of this procedure is to separate the non dissolved TC compounds from the dissolved TC compounds by centrifuging the water sample. The IC fraction of the sample is removed by the addition of 1+1 nitric acid to the particulate matter.

8.6.2 Shake the sample bottle and measure a maximum of 80 ml aliquot of the sample with a graduated cylinder. Pour the sample into two labeled volatile (VOA) vials. Verify that sample levels in each vial are equal to each other.

8.6.3 Centrifuge the VOA vials at a setting of '7' for 5 minutes.

8.6.4 Remove all of the water from each vial until approximately 10 ml remain in each vial.

8.6.5 Transfer all the material (water and particulates) from the two vials to one vial.

8.6.6 Centrifuge the vial with the water and particulates at a setting of '7' for 5 minutes.

8.6.7 Remove all the water from the vial. Set the 1000 µl Rainin pipet to 650 µl and transfer the particulates to a quartz boat.

Note: If all the material from the VOA vial will not fit inside the boat, transfer a portion of the material from the vial to the boat and dry the boat and the material inside the GC oven. Repeat the process of transferring the sample from the vial to the boat and drying the material until all the sample extract has been transferred to the boat.

8.6.8 Place the boat in the numbered aluminum weigh boat. Record the NEA #, volume of sample centrifuged and the boat number into the TOC logbook.

8.6.9 Add 2 to 3 drops of 1+1 nitric acid to each sample. Turn off the GC oven.. Place the aluminum weigh boats in the GC oven. Place a 60 ml beaker over each quartz boat. Turn on the GC oven. Remove samples when dried (minimum of 10 minutes).

8.6.10 Follow the instructions in **8.3.6** for analyzing samples.

8.6.11 The concentration of the samples must be within the range of the calibration curve. If the sample concentration was too high, extract less than 80 ml of the sample.

8.7 Set up and maintenance of the UV-Persulfate reaction module.

8.7.1 Refer to the instrument manual for specific instructions and part numbers for all components.

8.7.2 Connect the tubing from the oxygen tank to the 'Carrier in' port. Connect the tubing from the 'Carrier out' port to the 'In' port of the NDIR detector module.

8.7.3 For the UV lamp, a thin film of Teflon fabricated in a conical shape is placed over the taper joint. Any excess is trimmed back from the top and bottom ends of the joint with a razor blade.

8.7.4 The position of the lamp should be adjusted so that the reactor coils just clears the fritted glass gas dispenser. Carefully insert the cap and lamp assembly into the reactor and check the clearance to the fritted gas dispenser. The lamp is held together by two springs.

8.7.5 Install the lamp so that the carrier gas exit tube is pointing to the front. The reactor is held in place by a three prong grip utility clamp.

8.7.6 **Reactor Liquid Plumbing.** Connections are made between the ports on the inside of the right side of the module to the reactor and other ports inside the reactor with Teflon lines and red/white septums. The ports on the inside of the module are counted one through six starting with one near the top of the case.

8.7.7 Connect the Teflon line from port 1 to the waste drain port of the reactor (the top of the "U" tube on the right side of the reactor). The 1/16" line should be pushed down through the septum about one inch and later adjusted up or down in the side arm so that the liquid level is about 1/4" above the inlet of the recycle arm.

8.7.8 Connect the line from port 2 to the recycle arm of the reactor. This port is located near the upper-center and points upward. Plug the horizontal port of this side arm with a red/white septum without a hole.

8.7.9 Connect the free line from the injection port to the sample inlet port at he bottom-left of the reactor body. Insert the Teflon tubing almost all the way through the glass capillary section of the inlet port.

8.7.10 **Reactor Gas Plumbing and Liquid Trap Plumbing.**

8.7.11 Connect 1/8" Teflon line from port 4 to the gas inlet at base of reactor with a red/white septum.

8.7.12 Mount liquid trap "U"" tube to the left of the reactor and run drain line to a beaker under the reactor.

8.7.13 Connect 1/8" Teflon line from outlet port of reactor cap to top inlet port of liquid trap with a red/white septum at reactor end and a gray perforated septum at the "U" tube end. Push line at the "U" tube inlet through septum hole until it is just below top of bulb.

8.7.14 Connect 1/8" Teflon line from permeation drier (top left of the interior of the module to the angled port of the "U" tube) with a gray perforated septum.

8.7.15 **Reaction Module Pump Tube Installation and Pump Adjustment.**

8.7.16 Release the pump tube pressure fingers by pressing on the upper part of the while plastic plate located toward the front of the pump assembly. This will release the pressure plate and allow the pressure fingers to rotate downward.

8.7.17 Install a green/green bridged tube at the inner most position. Install a black/black bridged tube in the second position. Install a black Viton purple/purple bridged tube in the third position.
Note: The pump pressure plate and fingers should be left in their operating position overnight to insure that reagent does not siphon out of the reactor.

8.7.18 Raise all four pressure fingers and raise the pressure plate so that the screws press up on the fingers. Push up on the bottom of the pressure plate and push in on the bottom of the white plastic locking block until it locks the pressure plate in place.

8.7.19 Connect a piece of plastic tubing to the back end of the green/green tubing. Place the free end of the plastic tubing into a container of laboratory water. Turn on the pump. Slowly adjust the screw for the green/green tube inward until the water just starts to rise in the tube. Advance the screw one-half turn more.

8.7.20 Repeat the procedure for the black/black and purple/purple tubes.

8.7.21 **Reactor External Plumbing.** The pump tube inlets are to the rear, outlets to the front. Connections between the pump tubing and module tubing are made on the ports <u>outside</u> the module.

8.7.22 Connect the inlet of the green/green pump tube to port 1 with 1/8" Teflon line. Connect a 1/8" Teflon line to the outlet of the green/green pump tube and place the end of the line in a waste container on the bench top.

8.7.23 Connect a 1/16" Teflon line to the inlet of the black/black pump tube and place the end of the line in the 2.0% $K_2S_2O_8$ solution.

8.7.24 Connect a 1/16" Teflon line between port 3 and the exit side (left) of the mixing tee. Connect a 1/16" Teflon line between the outlet of the black/black pump tube and the top of the mixing tee. Connect a 1/8" Teflon line between the outlet of the purple/purple pump tube and the mixing tee.

8.7.25 Connect a 1/8" Teflon line between port 2 and the outlet of the purple/purple pump tube.

8.8 Operation and calibration of the UV-persulfate and IR-I NDIR detector modules.

8.8.1 The blue injection septum must be replaced after approximately 100 injections have been made. Replace the blue septum in the injection port before starting the flow of reagent through the module.

8.8.2 Because there is a low flow of reagent(s) to the reactor, gently remove the top of the reactor and pour 2.0% $K_2S_2O_8$ so that the time required to fill the reactor with reagent is decreased. The reactor should be approximately 2/3 full. Connect the top of the reactor.

8.8.3 Place the pressure plate on the pump tubes. Turn on the pump and lamp by pressing the three white power buttons.
<u>Caution</u>: Do not open the module door while lamp is on.

8.8.4 Turn on the NDIR detector. The level of reagent in the reactor recycle arm must be at the top of the arm before starting analysis. The baseline on the detector must also be stable before starting analysis.

8.8.5 Inject the calibration standards one at a time. Wait 15 seconds and Press the "Start" button. The instrument will 'beep' to indicate that the analysis is completed and is ready for the next injection. Repeat injection of the sample until consecutive measurements are obtained that are reproducible to within ± 10%.

8.8.6 For low level analysis, the amount of carbon inject into the instrument for the calibration standards should range from ~0.10 to 24 µg. This can be achieved by injecting different volumes of the calibration standards.

8.8.7 Enter the injection number, standard label, date analyzed, injection volume, and the area printed by the printer in the TOC logbook. See the **Glossary** for information about the correlation coefficient.

8.8.8 After the analysis is completed, flush the reactor system by placing the tubing for the 2.0 % $K_2S_2O_8$ in a container of RO water and turn the pump on for one hour.

8.9 The determination of TOC in water.

8.9.1 Remove the IC fraction of the sample by acidifying and sparging the preserved sample with nitrogen gas for 10 minutes.

8.9.2 Transfer a portion of the sample to a VOA vial and place in a test tube rack. Attach a Pasteur pipet to plastic tubing that is connected to a nitrogen tank.
Add three drops of concentrated H_3PO_4 to the sample and place the tip of the Pasteur pipet in the sample. Slowly turn on the gas flow to produce gentle bubbling inside the vial for 10 minutes. The sample is now ready for analysis.

8.9.3 Inject 0.100 ml of sample into the UV-persulfate module. Wait 15 seconds and Press the "Start" button. The instrument will 'beep' to indicate that the analysis is completed and is ready for the next injection. Repeat injection of the sample until consecutive measurements are obtained that are reproducible to within ± 10%.

8.9.4 The concentration of the samples must be within the range of the calibration curve. If the original concentration of the sample was too low, inject a larger volume of sample up to 0.25 ml. If the sample concentration was too high, inject a smaller volume down to 0.010 ml. If the sample concentration is still too high, dilute a portion of the unsparged sample and repeat **8.7.2** and re analyze the diluted sample.

8.9.5 Repeat **8.9.2-4** for the remaining samples.

8.9.6 Enter the injection number, standard label, date analyzed, injection volume, and the area printed by the printer in the TOC logbook.

8.10 Sample calculations utilizing Lotus spreadsheets.

8.10.1 After the instrument is calibrated, a Lotus spreadsheet is used to construct a calibration curve and the linear regression. Generate a spreadsheet each time that the instrument is calibrated for either water samples or solids.

8.10.2 Log into the network and access "Lotus 1-2-3". Recall a previous spreadsheet, see the following table for an example of the directories and examples of files saved on November 11, 1996.

Analyte (matrix)	Lotus directory	Example
TOC (solids)	S:\DATA\TOCS*.*	S:\DATA\TOCS\1118.WK6
TOC (water)	S:\DATA\TOC*.*	S:\DATA\TOC\1118.WK6
POC (water)	S:\DATA\POC*.*	S:\DATA\POC\1118.WK6

8.10.3 Enter the average area (subtract the average blank area) for the calibration standards in the box used for constructing the calibration curve. Update the linear regression. For the calibration curve, enter the date of analysis.
Note: Except for the lowest calibration standard, the percent recoveries for the calibration standards must be between 90 and 110%.

8.11 Quality control (see attachment B for corrective actions)

8.11.1 A calibration blank is required for each day of analysis. Check blanks are analyzed after every initial and continuing check standard. The concentration of the blank must be less than the MDL for that method.

8.11.3 **Sample duplicate:** A duplicate analysis is performed every 10 samples.
RPD = Abs. {(S1 - S2)/(S1 + S2)} X 200

8.11.4 **Independent and continuing calibration verification standard (ICV) and (CCV)**: A purchased TOC solution of known concentration is analyzed after each calibration curve is generated, after every 10 samples and at the beginning and end of the analysis.
The ICV/CCV is analyzed in replicate.
% recovery = (calculated value/certified value) x 100.

8.11.5 For soil samples, if the sample analyses was off scale <u>and</u> the minimum sample weight of 1.0 mg was used, calculate the maximum concentration of TOC based on the µg of carbon of the highest calibration standard, average sample weight, and the percent total solids. Report the results as <u>greater than</u> the calculated maximum sample concentration , the detection limit and the standard deviation

8.11.6 **Laboratory fortified sample matrix**. Perform a spike on every 20th soil or water sample. For water samples, spike 10 ml of the sample with an aliquot of the ICV/CCV standard and proceed as in **8.9.2-.4**. For soil samples, weigh the sample and proceed as in **8.4.1-.10**. Place the sample and boat in the boat sampler and spike the sample through the injection port with the ICV/CCV standard. The final concentration of the spiked sample must be within the calibration curve.
% recovery = {(spike sample conc.) - (sample conc.)}/(spike added) X 100

8.12 Entry of data into LIMs.

8.12.1 After the calibration curve has been completed, give the LIMs manager a copy of the Lotus spreadsheet for the calibration curve with the area for blank and area for the lowest standard used in the calibration curve.

8.12.2 Log into LIMS. Click "Win Results" or "Results" from LIMS toolbar. Select the appropriate samples by either typing in the sample ID's or selecting the Login Record File.

8.12.3 Choose the result entry template "TOCSOL", then click "OK". A result entry spreadsheet will then be created with the following columns: TOCSO, TOCI_A, TOCI_1, TOCI_2, TOC_1SW, TOC_2SW, %SOLIDS. To find out what should go into these QC data columns, right click on the column heading in gray at the top of the spreadsheet.

8.12.4 The data for samples should be entered into the columns as follows:

TOCI_1 = Area Counts for Sample

TOCI_2 = Area Counts for Sample Replicate

TOC_1SW = Sample weight in grams

TOC_2SW = Sample Replicate weight in grams

%SOLIDS = % Total Solids for Sample (Enter as a percentage, not a decimal)

TOCI_A = Average Area Counts for Sample (Fills in automatically)

TOCSO = Final result for TOC in Solids (Fills in automatically)

8.12.5 Once the field TOCSO has been filled in by the computer, right click on that field and select "detailed edit" from the pull down menu. Confirm that the MDL and the date analyzed for the sample are correct. Proceed to the next sample.

8.12.6 Once the data has been entered for all samples, go the QC section of the spreadsheet. If batching was performed correctly there should be some of these fields displayed in white. Right click on the dark gray fields in that same row so that all appropriate QC tests have been added.

(For example, if the sample has a duplicate be sure all the raw data fields for the duplicate have been turned white.) Enter in all appropriate QA/QC data.

9.0 REFERENCES

9.1 "Determination of Total Organic carbon in sediment," Lloyd Kahn, U.S.E.P.A. Region II, Edison NJ.

9.2 Application Note: TOC-011 "Analysis of sludges and solids for carbon," Tekmar-Dohrmann, Cincinnati, OH 10/95.

9.3 NYSDOH ELAP manual item #271, 4/15/94.

9.4 *Standard Methods for the Examination of Water and Wastes*, method #5310B, 17th edition. 1989.

10 ATTACHMENTS

10.1 **Attachment A**: Note pages for analyst.

10.2 **Attachment B**: Quality assurance and corrective action for problems associated with sample preparation and analysis.

10.3 Attachment C: Disposal of samples and waste.

ATTACHMENT A
NOTES

ATTACHMENT A CONTINUED
NOTES

ATTACHMENT B
QUALITY ASSURANCE AND CORRECTIVE ACTIONS.

Calibration curve: If the correlation coefficient is < 0.997 or if the recoveries for any of the calibration standards are not within 10% of the true value (except for the lowest standard), repeat injections of the outlying standards until curve is within acceptance criteria.

Independent calibration verification (ICV/QCS): Must be within 85 – 115% of true value. If the Percent recovery is not within the limits specified, recalibrate the instrument and reanalyze all samples since the last compliant continuing calibration verification standard.

Check standard (CCV/IPC): Use ICV solution as mentioned previously. Must be within 85 – 115% of true value. If the Percent recovery is not within the limits specified, recalibrate the instrument and reanalyze all samples since the last compliant continuing calibration verification standard.

Preparation blank: For TOC in water, prepare one blank consisting of laboratory grade water for each batch of samples sparged daily. Prepare blank as described in 8.91-3. If he average area of the blank is greater than the half the value of the lowest standard used to construct the calibration curve, prepare a new blank solution.

Check blank (CCB): For TOC in water, **see Preparation blank**. For TOC in solids, analyze 70 ul of laboratory grade water. Analyze the CCB solution after each ICV/CCV solution. If the average area of the blank is greater than the half the value of the lowest standard used to construct the calibration curve, determine the source of the problem, fix the problem and reanalyze all samples since the last compliant CCB.

Laboratory control sample: Not applicable

Sample duplicate: Prepare and analyze one sample duplicate for every 10th sample. For water samples, a control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to 5x the RDL. A control of +/- the RDL shall be used if either the sample or its duplicate is less than 5x the RDL. For soil samples, refer to the latest control limit for duplicates. If the the results for the sample and duplicate are unacceptable, a case narrative explaining why the RPD for a sample and its duplicate was outside the control limits must be written and approved by the quality assurance officer. A copy of the case narrative must be sent with the report to the client.

Matrix spike: Prepare and analyze one matrix spike for every 20th sample. **TOC**: For water and soil samples, refer to the latest control limit for matrix spikes. Spile with an aliquot of the ICV/CCV solution. If the results for the matrix spike is unacceptable, prepare and analyze another matrix spike. If the results for the matrix spike is still unacceptable, a case narrative explaining why the percent recovery for the matrix spike was outside the control limits must be written and approved by the quality assurance officer. A copy of the case narrative must be sent with the report to the client

Serial dilution: Not applicable

Analytical spike: Not applicable

Method of standard additions: Not applicable

Overrange samples: Dilute or redigest samples that are greater than the value of the highest standard used to prepare the calibration curve so that the results are within the calibration curve.

ATTACHMENT C:
DISPOSAL OF SAMPLES AND WASTE

1. Refer to SOP NE054 for procedures for disposing of laboratory waste.

2. Acidified aqueous samples and extracts that do not contain metals or organic compounds above 0.050 mg/L, can be neutralized to a pH above 4.0 before disposal.

3. All client sample containers must be defaced with a permanent marker before disposal.

11 GLOSSARY

11.1 **Laboratory control.:** A standard of known concentration that is independent of the standards used for quantifying samples.

11.2 **Continuing calibration standard (CCV):** Used to assure calibration accuracy during each analysis run. It must be run at a frequency of 10% during the run. It must also be analyzed at the beginning and the end of the run. Its concentration must be at or near the mid-range level of the calibration curve.

11.3 **Correlation coefficient:** The correlation coefficient for the calibration curve must be greater than or equal to 0.997 according to NYSDOH requirements.

APPENDIX A-97

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF NON-FILTERABLE RESIDUE ACCORDING TO EPA 1979 METHOD 160.2

STANDARD OPERATING PROCEDURE

Author: John Nicpon

Reviewed by:

Northeast Analytical, Inc.
Issuing section: Inorganics laboratory
NE117_02.SOP
Date: February 25, 2002
Revision Number: 2

William A Kotas
Quality Assurance Officer

Robert E. Wagner
Laboratory Director

1.0 TITLE

Standard operating procedure for the determination of non-filterable residue (or total suspended solids) according to EPA 1979 method 160.2.

2.0 PURPOSE

The purpose of this SOP is to provide procedures analyzing water samples for suspended solids.

3.0 SCOPE

This method is applicable to waste water and ground water.

4.0 COMMENT

Residue , non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103 - 105 ^{O} C. A measured volume of sample is passed through a preweighed crucible that contains a glass fiber filter. The crucible is dried in a oven and the change in weight is determined. The concentration of non filterable solids is calculated by dividing the difference in the crucible weight by the volume of sample filtered.

The holding time for analyzing samples is seven days from the date that the sample was collected. The detection limit for samples is dependent on the amount of sample filtered. If a client requires the lowest detection limit possible, the entire sample bottle is to be used.

Because the method is based on gravimetric measurements, handle the crucibles with tweezers or with vinyl gloves.

5.0 SAFETY

All safety precautions associated with the preparation and analysis of samples must be followed. Gloves and protective eyeware are required.

6.0 REQUIREMENTS

6.1 Method detection limit study

6.1.1 Analyze eight samples (use ERA control samples or other vendor) and a blank according to the procedures set forth in this document. Calculate the MDL by multiplying the standard deviation of eight MDL measurements by 2.998. For the MDL to be valid, it must be greater than 1/10 the amount spiked but not greater than the amount spiked.

6.2 Precision and accuracy studies

6.2.1. Each analyst must demonstrate the ability to generate acceptable results with this method using the following procedure.

6.2.2 Spike four precision and accuracy samples for the analytes of interest at a level at least ten times the PQL level.

6.3 Knowledge on the operation and calibration of the analytical balance is required.

6.4 Knowledge on the operation of the drying oven located in the Inorganics laboratory.

6.5 Knowledge on the maintenance of the portable desiccator box.

6.6 Knowledge on the operation and maintenance of the vacuum pump.

7.0 EQUIPMENT

7.1 Equipment

7.1.1 Small vacuum pump. Located in the Inorganics laboratory.

7.1.2 Large vacuum pump. Located in the Inorganics laboratory.

7.1.3 One liter Erlenmeyer vacuum flasks with crucible holder and glass insert. (Baxter p/n F4375-1L or equivalent). Located in the Inorganics laboratory.

7.1.4 Glass fiber filters. (Baxter p/n F2835-24 or equivalent). Located in the Inorganics laboratory.

7.1.5 Tweezers. Located in the Inorganics laboratory.

7.1.6 Drying oven. Set at a temperature of 103 -105 ^{O}C. Located in the Inorganics laboratory.

7.1.7 Rinse bottle. Filled with laboratory grade water. Located in the Inorganics laboratory.

7.1.8 500 and 250 ml graduated cylinders. Located in the Inorganics laboratory.

7.1.9 Total suspended solids logbook. Located in the Inorganics laboratory.

7.1.10 Crucibles. (VWR p/n 23835-113 or equivalent)

7.2 Reagents and Standards

7.2.1 Laboratory grade water. Located in the cooler room.

7.2.2 Laboratory control sample. Talc. (Fisher p/n T2-500 or equivalent) Located in the Inorganics chemical shelf. Prepare a 100 mg/L solution for the Laboratory control sample.

8.0 PROCEDURE

8.1 Operation and maintenance of vacuum pumps.

8.1.1 Before using vacuum pumps, check that the minimum volume of pump oil is in the pump oil reservoir. For both pumps, empty the collection flasks frequently to prevent water from entering the pump. For the large vacuum pump, a water trap is used to prevent water from entering the pump. Empty the water trap when necessary.

8.1.2 To operate the large vacuum pump, connect the collect flasks to the vacuum hoses. Before operating the pump the vacuum hoses should be in the closed position. Place the crucibles on the flasks, turn on the pump, turn the desired vacuum hose to the open position and proceed to filter samples as described in **8.5.**

8.1.3 To operate the small vacuum pump, connect the vacuum hose to the pump to the hose connection on the pump. Place the crucible on the flask, turn the pump on, and proceed to filter the sample as describe in **8.5.**

8.2 Oven operation.

8.2.1 Before placing crucibles in the oven, the temperature of the oven must be between 103 and 105 °C. Check the calibrated thermometer in the glass bottle inside the oven for the oven temperature. Adjust the temperature of the oven if necessary, by slightly turning the control knob. Wait five minutes, check the temperature, repeat the adjustment process until the temperature is within the required temperature range.

8.3 Operation and maintenance of portable desiccator box.

8.3.1 After the crucibles are removed from the oven, they must be placed in the portable desiccator box before they are weighed. The purpose of the desiccator box is to prevent the crucibles from absorbing moisture while they are cooling.

8.3.2 The desiccant material must be dried in the drying oven when the color of the material is a pale blue. Pour the material into a drying pan and placed in the drying oven for a minimum of one hour. Transfer the material to the portable desiccator box, and wait a minimum of one hour for the material to cool to room temperature before placing crucibles in the desiccator box.

8.4 Total suspended solids logbook and preparation of crucibles.

8.4.1 For each day of analysis, a new page of the logbook must be used. Write the date, analyst initials and the 'TSS' at the top of the page. Set up columns with the labels of 'Crucible #", 'Initial wt. (g)', 'Final wt. (g)', 'NEA #', 'Sample volume (ml)', 'mg/L', and 'D.L. (mg/L)'.

8.4.2 The crucibles must be labeled with identification numbers that allows the analyst to identify the crucibles. Place the desired number of crucibles in a glass drying pan. Place filters into the crucibles with tweezers. The rough side of the filter should be facing up. Using the tweezers, place the crucibles on the collection flasks that are connected to the vacuum pump. Turn the pump on and wet the filter with an aliquot of water from the squirt bottle. **Note:** The filter must cover all the holes of the crucible. Turn off the pump and repeat the process with the next crucible. If a hole appears in the filter, replace the filter and repeat the process. Place the crucibles into the drying pan and place the pan in the drying oven for a minimum of three hour. Prepare extra crucibles with each batch.

8.4.3 Remove the crucibles from the oven and place in the portable desiccator box. Wait one hour, and weigh the crucibles on the analytical balance. Record the crucible number and the initial weight (grams) in the logbook. Using Lims record the intial weight in the appropriate location.

8.5 Sample analysis

8.5.1 Remove the samples from the cooler or refrigerator.

8.5.2 If the entire container of sample is to be filtered, mark the volume level with a marker.

8.5.3 The weight of captured residue on the filter must be greater than 1.0 mg. Generally, a sufficient volume of sample is filtered so that a sufficient amount of solid material covers the filter without clogging the filter. If a client requires the lowest detection limit possible, the entire sample bottle is to be used.

8.5.4 Place the crucible on the collection flask, and record the sample number in the logbook. Turn the pump on and squirt RO water onto the filter. Shake the sample bottle and pour into a 100 ml graduated cylinder. Record the volume (ml), and pour the sample onto the filter.

8.5.5 If the additional sample is required for filtering, repeat **8.5.4**. For samples that require the filtration of the complete sample bottle, pour directly from the bottle into the crucible

8.5.6 Do not overfill the crucible. If the filter clogs, repeat the analysis with a different crucible and use less sample.

8.5.7 After the sample has passed through the filter, rinse the graduated cylinder with aliquots of RO water and pour onto the filter. Rinse filter with several aliquots of RO water from rinse bottle. Turn off the pump and place the crucible into the drying oven. If the entire sample bottle was used, fill the bottle to the mark with water, pour into a graduated cylinder and record the volume.

8.5.8 The crucibles must be in the drying oven a minimum of one hour. Take the crucibles out of the drying oven and follow **8.4.3** and record the final weight (grams) in the logbook.

8.6 Calculations

8.6.1 To calculate the non filterable residue weight (grams), divide the difference of the initial weight and the final weight of the crucible by the total sample volume (ml), and multiply by 1,000,000. Report the result to two significant figures (mg/L).

8.6.2 To calculate the detection limit for the sample, divide 1000 by the sample volume (ml), and report the result to two significant figures (mg/L).

8.7 Quality control

8.7.1 A sample blank is analyzed on each day of analysis. Filter 1000 ml of RO water through one of the crucibles. The calculated value for the blank must be less than 1.00 mg/L. If the result is unacceptable, repeat **8.5.8** for all the samples associated with the blank. If the result is still unacceptable, repeat **8.4** through **8.6** for all samples associated with the blank.

8.7.2 A laboratory control is analyzed on each day of analysis. From the certified value given, filter enough sample for accurate determination. If the result is outside the recovery limits supplied with the control, repeat **8.5.8** for all the samples associated with the control. If the result is still unacceptable, repeat **8.4** through **8.6** for all samples associated with the control. Record the percent recovery on the logbook page.
% recovery = (calculated value/certified value) X 100

8.7.3 A sample duplicate is analyzed on each day of analysis or every ten samples, which ever is more frequent. If additional sample is unavailable for duplicate analysis, analyze the laboratory control a second time. Calculate the relative percent difference (RPD). The limit for RPD is 20 %. If the result is unacceptable, repeat **8.5.8** for all the samples associated with the duplicate. If the result is still unacceptable, repeat the analysis of the samples associated with the duplicate. Record the RPD on the notebook page.
RPD = Abs. {(S1 - S2)/(S1 + S2)} X 200

8.7.4 Sample results, detection limits, NEA numbers and the date of analysis are entered into LIMS.

LIMS RESULT TEMPLATE “TSS” COLUM HEADINGS AND DESCRIPTIONS

Column	Description	Column	Description	Column	Description
INTWGT	Initial wt.: sample	**FINWGT**	Final wt. :sample	**TOTVOL**	Total vol.: sample
TSSI	TSS intermediate cal.	**TSS**	Sample result	**TSS_LIW**	Initial wt.: LCS
B_TSS	Blank result	**D_TSS**	Duplicate sample result	**P_TSS**	Precision calculation
L_TSS	LCS % recovery	**TSS-BFW**	Final wt.: blank	**TSS_BIN**	Blank intermediate cal.
TSS_BV	Total vol.: blank	**TSS_DF**	Final wt.: Duplicate	**TSS_DIN**	Dup. Intermediate cal.
TSS-DV	Total vol. Duplicate	**TSS-LFW**	Final wt.: LCS	**TSS_LIN**	LCS intermediate cal.
A_TSS	True value: LCS	**LITSS**	LCS result	**TSS_DIW**	Initial wt.: Duplicate
TSS_LV	Total vol.: LCS	**TSS_BIW**	Initial wt.: Blank		

8.7.5 Analyst must read, understand, and use the latest version of the laboratory's SOPs that relate to their job responsibilities. The SOPs must be read during their initial training, annually, and when the SOPs are revised.

8.7.6 After the completion of the analysis run, the analyst reviews the logbook(s) and the analytical data for completion.

8.7.8 The supervisor/designee reviews the logbook(s) and data and records their initials and revew dates on the appropriate documents.

8.7.9 Each QC measurement is reviewed and compared to the appropriate acceptance criteria.

8.7.10 If the acceptance criteria for QC measures has been exceeded for requested analytes and the data is to be reported, the following procedures must be implemented:
8.7.10.1 The quality assurance officer must be notified.
8.7.10.2 The data must be flagged with the appropriate qualifiers and case narrative.
8.7.10.3 The client must be notified about the data.

9.0 REFERENCES

9.1 "Methods of Chemical Analysis of Water and Wastes'," EPA-60/4-79-020, revised March 1983. method # 160.2

9.2 NYSDOH Environmental Laboratory Approval Program Manual item # 271.

10.0 ATTACHMENTS

10.1 **Attachment A**: Summary of procedure for TSS.

ATTACHMENT A

Summary of procedure for TSS

1. Prepare crucibles and place in oven for a minimum of one hour.

2. Remove crucibles from oven and place in desiccator for one hour, weigh crucibles.

3. If client requires entire sample for analysis, mark bottle, else pour portion of sample into 500 ml graduated cylinder.

4. Record volume, place crucible on flask, turn on pump, and pour sample into crucible.

5. Pour additional sample into crucible until sufficient material has collected on top of filter.

6. Place crucibles in oven for a minimum of one hour, place crucibles in desiccator for one hour.

7. Weigh crucibles and calculate results (mg/L) and detection limits (mg/L) to two significant figures.

8. Q.C.: A blank and control for each day of analysis. A sample duplicate on each day of analysis, or every 10 samples.

9. Q.C. sheets for clients requesting documentation: Control and duplicate calculations.

10. Client certificates for clients requesting documentation: Analyst generates certificates using LIMS.

11. Client folders: A copy of notebook page and data result sheet.

11.0 GLOSSARY

11.1 **Residue , non-filterable:** those solids that which are retained by a glass fiber filter and dried to constant weight at 103 -105 ° C.

11.2 **Laboratory control.:** A standard of known concentration that is independent of the standards used for the quantifying samples. It is analyzed at a frequency of once a day.

APPENDIX A-98

TEST METHOD FOR PARTICLE-SIZE ANALYSIS OF SOILS

GeoTesting Express, Inc.

Standard Operating Procedure

ASTM D 422

Technical Information

Reference Number:	ASTM D 422
Test Method Title:	Test Method for Particle-Size Analysis of Soils
Test Property:	Grain size analysis
Test Specimen Size:	Passing #10 sieve: 115 g for sandy soils, 65 g for silty or clayey soils Retained on #10 sieve: see test standard (based on largest particle size)
Number of Test Specimens:	1 (representative sample obtained by quartering, mixing or splitting
Test Equipment:	Stirring apparatus A Hydrometer (ASTM) Sedimentation Cylinder Drying containers Balance readable to 0.01 gram for material passing #10 sieve or 0.1% of mass for material retained on #10 sieve Thermometer readable to 0.5 • C Various sieves 250 mL beaker Drying oven capable of maintaining a temperature of 110 ± 5 • C Dispersing agent mixture (40 g/L of Sodium Hexametaphosphate solution) Mechanical sieve shaker

Standard Operating Procedure

Sieve analysis of portion retained on #10 sieve

1. Separate the portion retained on #10 sieve into a series of fractions using various sieve sizes ranging from 3 inch to #10. Set up in mechanical shaker and shake for 10 minutes. Determine the mass retained on each sieve by weighing and recording mass to nearest 0.1 % of sample mass.

Hydrometer and sieve analysis of portion passing #10 sieve

2. Place appropriate size sample in a 250 mL beaker. Cover with 125 mL of dispersing agent mixture. Stir and allow to soak for at least 16 hours.

3. Disperse the solution further by using Stirring apparatus A. Add distilled water as needed to fill cup to the half. Stir 1 minute.

4. Immediately after dispersion, transfer slurry to a sedimentation cylinder. Add distilled water to 1000 mL point. Use rubber stopper over the open end and turn the cylinder upside down and back for a period of 1 minute (should be 60 turns per minute). Set the cylinder down and begin to

take and record hydrometer readings at the following intervals: 1, 2, 4, 8, 15, 30, 60, 120, 240 and 1440 minutes. After each reading, the temperature of the solution should be recorded.

5. After the final hydrometer reading, transfer the suspension to a #200 sieve and wash with tap water until effluent water is clear. Transfer material to a container and dry in oven to constant mass at 110 ± 5 •C. After drying, sieve the remaining material in shaker using desired number of sieves for 10 minutes. Record mass retained on each fraction to nearest 0.01 g.
6. Calculations: use GLMS software to enter data and calculate % passing and retained for each sieve size and hydrometer readings.
7. Report: sample identification, sample description, percentage passing or retained on each sieve fraction (tabular and graphical).

APPENDIX A-99

STANDARD TEST METHOD FOR INTERFACIAL TENSION OF OIL AGAINST WATER BY THE RING METHOD

Designation: D 971 - 82

An American National Standard

Standard Test Method for
INTERFACIAL TENSION OF OIL AGAINST WATER BY THE RING METHOD[1]

This standard is issued under the fixed designation D 971: the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This method covers the measurement of, under nonequilibrium conditions, the interfacial tension of mineral oils[2] against water.

2. Summary of Method

2.1 *Interfacial Tension* is determined by measuring the force necessary to detach a planar ring of platinum wire from the surface of the liquid of higher surface tension, that is, upward from the water-oil interface. To calculate the interfacial tension, the force so measured is corrected by an empirically determined factor which depends upon the force applied, the densities of both oil and water, and the dimensions of the ring. Measurements are made under rigidly standardized nonequilibrium conditions in which the measurement is completed within 1 min after formation of the interface.

3. Significance and Use

3.1 This method has been shown by practice to give a reliable indication of the presence of hydrophilic compounds.

4. Apparatus (Figs. 1 and 2)

4.1 *Tensiometer*[3] with a torsion wire to apply the force to lift the ring; the torsion wire is attached to a scale graduated in millinewtons per metre.

4.2 *Ring* of fine platinum wire in a nearly true circle of 4 or 6-cm circumference welded to a suitable stirrup made of the same wire. It is necessary to know, to three significant figures, the circumference of each ring, and the ratio of the diameter of the ring to the diameter of the wire of which it is made.

4.3 *Sample Container*[4]—Glass beaker or cylindrical vessel having a minimum diameter of 45 mm.

5. Preparation of Apparatus

5.1 Clean all glassware by removing any residual oil with petroleum naphtha followed by several washes with methyl ethyl ketone and water and immersion in a hot cleaning solution of chromic acid. (**Warning**—Petroleum naphtha and methyl ethyl ketone are flammable and harmful if inhaled. Chromic acid can cause severe burns and requires extreme care. See Annex A1.1 and A1.2 for precautions in using these materials.) Rinse thoroughly with tap water and then with distilled water. Unless it is to be used immediately, drain the sample container in an inverted position over a clean cloth.

5.2 Clean the platinum ring by rinsing it in petroleum naphtha followed by rinsing in methyl ethyl ketone. (**Warning**—See Annex A1.3.) Then heat the ring in the oxidizing portion of a gas flame.

6. Calibration of Apparatus

6.1 Calibrate the tensiometer against known weights and adjust its zero point according to

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[1] This method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants.

Current edition approved Aug. 27, 1982. Published October 1982. Originally published as D 971 - 48 T. Last previous edition D 971 - 50 (1977).

[2] Statements defining this test and its significance when applied to electrical insulating oils of mineral origin will be found in ASTM Method and Specifications D 177, Testing Electrical Insulating Oils of Petroleum Origin. *1982 Annual Book of ASTM Standards*, Part 40.

[3] Tensiometers that use the Du Nouy principle for measuring interfacial and surface tension should be used.

[4] Plasticizers used in the manufacture of tubing and containers can be detrimental to the quality of distilled water.

the procedure of its manufacturer. Make certain that all portions of the ring are in the same horizontal plane.

7. Sample

7.1 Filter the sample through a 150-mm diameter, unwashed filter paper of medium porosity, using fresh paper for each 25-mL portion of oil. Determine the density of the filtered oil to the nearest 0.001 g/mL at 25°C.

8. Procedure

8.1 Introduce 50 to 75 mL of distilled water at a temperature of 25 ± 1°C to a freshly cleaned sample container and place it on the adjustable platform of the tensiometer. Clean the platinum ring (5.2) and suspend it from the tensiometer. Raise the adjusting platform until the ring is immersed in the water to a depth not exceeding 6 mm in the center of the sample container as determined by visual observation.

8.2 Slowly lower the platform, increasing the torque of the ring system by maintaining the torsion arm in the zero position. As the film of water adhering to the ring approaches the breaking point, proceed slowly with adjustment to assure that the moving system will be in the zero position when rupture occurs. Using the scale reading at which this occurs, calculate the tension of the water sample as described in Section 9 using the value 0.997 for the difference of density of water and air ($D - d$); a value of 71 to 72 mN/m should be obtained. When low values are found, possibly due to improper adjustment of the tensiometer or improperly cleaned apparatus, make readjustments; clean the sample container with hot chromic acid cleaning solution, rinse, and repeat the measurement. If a low value is still obtained, further purify the distilled water (for instance, by redistilling from an alkaline solution of potassium permanganate).

8.3 Return the tensiometer scale to zero and raise the adjustable platform until the ring is immersed to a depth of about 5 mm in the distilled water. Pour the filtered oil, previously brought to a temperature of 25 ± 1°C on the water to a depth of about 10 mm. Take care that the ring does not touch the oil-water interface. If a ring with a short stirrup is used, keep the oil level below the top of the stirrup to prevent bridging. If this is not possible, break the bridge with a suitable clean, sharp instrument as soon as possible after withdrawing the stirrup from the oil.

8.4 Allow the oil-water interface to age for 30 ± 1 s, then slowly lower the platform, increasing the torque of the ring system by maintaining the torsion arm in the zero position. As the water adhering to the ring approaches the breaking point, proceed slowly with adjustment to assure that the moving parts will be in zero position when rupture occurs. Time these operations so that, as nearly as possible, 30 s are required to draw the ring through the interface. Proceed very slowly as the breaking point is approached, since the break is usually sluggish and too rapid movement may result in a high reading. Complete the entire operation, from the time of pouring the oil into the sample container until the film ruptures, in about 1 min. Record the scale reading at which the ring breaks free from the interface.

9. Calculation

9.1 Calculate the interfacial tension of the sample by means of the following equation;

$$\text{Interfacial tension, mN/m} = P \times F$$

where:

P = scale reading when film ruptures, mN/m (Note), and
F = factor converting scale reading in mN/m to interfacial tension obtained as described in 9.2.

NOTE—If the scale is not graduated in millinewtons per metre, or if either the ring or the platinum wire are of different diameters than those for which the scale is graduated, correct the scale readings to millinewtons per metre for the particular ring used.

9.2 Using the value of diameter ratio, R/r, specified by the manufacturer for the rings used, prepare a graph[5] of correction factors, F, by means of the following equation; the graph should cover even increments of $P/D - d$ from 0 to 800 and should give correction factors to three digits:

$$F = 0.7250 + \sqrt{\frac{1.452P}{C^2(D-d)} + 0.04534 - \frac{1.679}{R/r}}$$

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[5] For a description of procedure, see Zuidema and Waters, *Industrial and Engineering Chemistry*, Analytical Edition, IENAA, Vol 13, 1941, p. 312.

where:

P = scale reading, mN/m,
C = circumference of ring, mm,
D = density of water at 25°C, g/mL,
d = density of sample at 25°C, g/mL,
R = radius of ring, mm, and
r = radius of wire of ring, mm.

10. Precision

10.1 Results should not differ from the mean by more than the following amounts:

10.1.1 *Repeatability* (same operator and apparatus)— 2 % of mean.

10.1.2 *Reproducibility* (different operators and apparatus)—5 % of mean.

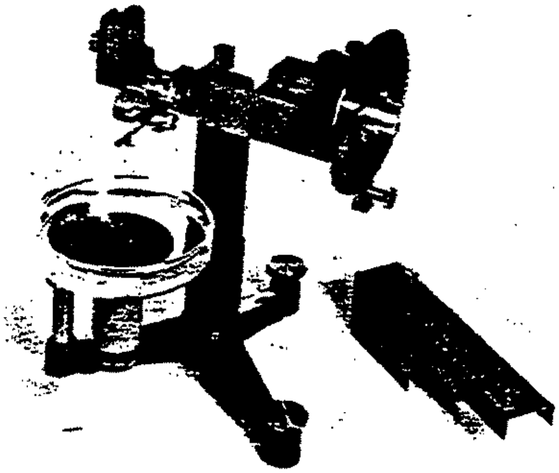

FIG. 1 Tensiometer

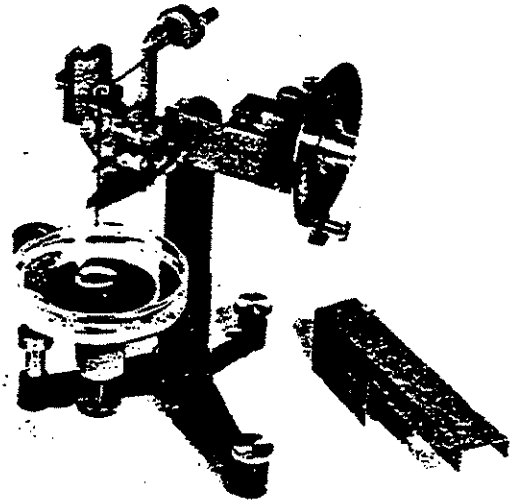

FIG. 2 Interfacial Tensiometer

ANNEX

(MANDATORY INFORMATION)

A1. PRECAUTIONARY STATEMENTS

A1.1 Petroleum Naphtha

Tag Closed Flash Point over 100°F. **Caution**—Combustible. Vapor harmful.
Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Avoid breathing vapor or spray mist.
Avoid prolonged or repeated contact with skin.

Tag Closed Cup Flash Point 20 to 100°F. **Warning**—Flammable. Harmful if inhaled.
Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Avoid prolonged breathing of vapor or spray mist.
Avoid prolonged or repeated skin contact.

A1.2 Methyl Ethyl Ketone

Warning—Flammable.
Keep away from heat, sparks, and open flame.
Keep container closed.
Use only with adequate ventilation.
Avoid prolonged breathing of vapor or spray mist.
Avoid prolonged or repeated contact with skin.

A1.3 Chromic Acid (Cleaning Solution)

Danger—Causes severe burns. A recognized carcinogen.

Strong oxidizer, contact with other material may cause fire. Hygroscopic.
Do not get in eyes, on skin, or on clothing.
Avoid breathing vapor or mist.
Keep container closed.
Use with adequate ventilation.
Do not take internally.
Wash thoroughly after handling.

APPENDIX A-100

STANDARD TEST METHOD FOR DENSITY AND RELATIVE DENSITY OF LIQUIDS BY DIGITAL DENSITY METER

Designation: D 4052 – 96

An American National Standard

Designation: 365/84(86)

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Method for
Density and Relative Density of Liquids by Digital Density Meter[1]

This standard is issued under the fixed designation D 4052; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This method was adopted as a joint ASTM-IP standard in 1984.

1. Scope

1.1 This test method covers the determination of the density or relative density of petroleum distillates and viscous oils that can be handled in a normal fashion as liquids at test temperatures between 15 and 35°C. Its application is restricted to liquids with vapor pressures below 600 mm Hg (80 kPa) and viscosities below about 15 000 cSt (mm^2/s) at the temperature of test.

1.2 This test method should not be applied to samples so dark in color that the absence of air bubbles in the sample cell cannot be established with certainty. For the determination of density in crude oil samples use Test Method D 5002.

1.3 The accepted units of measure for density are grams per millilitre or kilograms per cubic metre.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Note 1 and Note 2.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]
D 1250 Guide for Petroleum Measurement Tables[3]
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[4]
D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[4]
D 4377 Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration[4]
D 5002 Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *density*—mass per unit volume at a specified temperature.

3.1.2 *relative density*—the ratio of the density of a material at a stated temperature to the density of water at a stated temperature.

4. Summary of Test Method

4.1 A small volume (approximately 0.7 mL) of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.

5. Significance and Use

5.1 Density is a fundamental physical property that can be used in conjunction with other properties to characterize both the light and heavy fractions of petroleum and petroleum products.

5.2 Determination of the density or relative density of petroleum and its products is necessary for the conversion of measured volumes to volumes at the standard temperature of 15°C.

6. Apparatus

6.1 *Digital Density Analyzer*—A digital analyzer consisting of a U-shaped, oscillating sample tube and a system for electronic excitation, frequency counting, and display. The analyzer must accommodate the accurate measurement of the sample temperature during measurement or must control the sample temperature as described in 6.2. The instrument shall be capable of meeting the precision requirements described in this test method.

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricantsand is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

Current edition approved Apr. 10, 1996. Published June 1996. Originally published as D 4052 – 81. Last previous edition D 4052 – 95.

[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 05.01.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

[5] *Annual Book of ASTM Standards*, Vol 05.03.

6.2 *Circulating Constant-Temperature Bath,* (optional) capable of maintaining the temperature of the circulating liquid constant to ±0.05°C in the desired range. Temperature control can be maintained as part of the density analyzer instrument package.

6.3 *Syringes,* at least 2 mL in volume with a tip or an adapter tip that will fit the opening of the oscillating tube.

6.4 *Flow-Through or Pressure Adapter,* for use as an alternative means of introducing the sample into the density analyzer either by a pump or by vacuum.

6.5 *Thermometer,* calibrated and graduated to 0.1°C, and a thermometer holder that can be attached to the instrument for setting and observing the test temperature. In calibrating the thermometer, the ice point and bore connections should be estimated to the nearest 0.05°C.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] 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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

7.3 *Water,* redistilled, freshly boiled and cooled reagent water for use as a primary calibration standard.

7.4 *Petroleum Naphtha*[7] for flushing viscous petroleum samples from the sample tube.

NOTE 1—Extremely flammable.

7.5 *Acetone,* for flushing and drying the sample tube.

NOTE 2—**Warning:** Extremely flammable.

7.6 *Dry Air*—for blowing the oscillator tube.

8. Sampling, Test Specimens, and Test Units

8.1 Sampling is defined as all the steps required to obtain an aliquot of the contents of any pipe, tank, or other system, and to place the sample into the laboratory test container. The laboratory test container and sample volume shall be of sufficient capacity to mix the sample and obtain a homogeneous sample for analysis.

8.2 *Laboratory Sample*—Use only representative samples obtained as specified in Practices D 4057 or D 4177 for this test method.

8.3 *Test Specimen*—A portion or volume of sample obtained from the laboratory sample and delivered to the density analyzer sample tube. The test specimen is obtained as follows:

8.3.1 Mix the sample if required to homogenize. The mixing may be accomplished as described in Practice D 4177 (Section 11) or Test Method D 4377 (A.1). Mixing at room temperature in an open container can result in the loss of volatile material, so mixing in closed, pressurized containers or at sub-ambient temperatures is recommended.

8.3.2 Draw the test specimen from a properly mixed laboratory sample using an appropriate syringe. Alternatively, if the proper density analyzer attachments and connecting tubes are used then the test specimen can be delivered directly to the analyzer's sample tube from the mixing container.

9. Preparation of Apparatus

9.1 Set up the density analyzer and constant temperature bath following the manufacturer's instructions. Adjust the bath or internal temperature control so that the desired test temperature is established and maintained in the sample compartment of the analyzer. Calibrate the instrument at the same temperature at which the density of the sample is to be measured.

NOTE 3—**Caution:** Precise setting and control of the test temperature in the sample tube is extremely important. An error of 0.1°C can result in a change in density of one in the fourth decimal.

10. Calibration of Apparatus

10.1 Calibrate the instrument when first set up and whenever the test temperature is changed. Thereafter, conduct calibration checks at weekly intervals during routine operation.

10.2 Initial calibration, or calibration after a change in test temperature, necessitates calculation of the values of the constants A and B from the periods of oscillation (T) observed when the sample cell contains air and redistilled, freshly boiled and cooled reagent water. Other calibrating materials such as *n*-nonane, *n*-tridecane, cyclohexane, and *n*-hexadecane (for high temperature applications) can also be used as appropriate.

10.2.1 While monitoring the oscillator period, T, flush the sample tube with petroleum naphtha, followed with an acetone flush and dry with dry air. Contaminated or humid air can affect the calibration. When these conditions exist in the laboratory, pass the air used for calibration through a suitable purification and drying train. In addition, the inlet and outlet ports for the U-tube must be plugged during measurement of the calibration air to prevent ingress of moist air.

10.2.2 Allow the dry air in the U-tube to come to thermal equilibrium with the test temperature and record the T-value for air.

10.2.3 Introduce a small volume (about 0.7 mL) of redistilled, freshly boiled and cooled reagent water into the sample tube from the bottom opening using a suitable syringe. The test portion must be homogeneous and free of even the smallest air or gas bubbles. The sample tube does not have to be completely full as long as the liquid meniscus is beyond the suspension point. Allow the display to reach a steady reading and record the T-value for water.

10.2.4 Calculate the density of air at the temperature of test using the following equation:

$$d_a, \text{ g/mL} = 0.001293[273.15/T][P/760] \quad (1)$$

where:

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[6] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[7] Suitable solvent naphthas are marketed under various designations such as "Petroleum Ether," "Ligroine," or "Precipitation Naphtha."

T = temperature, K, and
P = barometric pressure, torr.

10.2.5 Determine the density of water at the temperature of test by reference to Table 1.

10.2.6 Using the observed T-values and the reference values for water and air, calculate the values of the Constants A and B using the following equations:

$$A = [T_w^2 - T_a^2]/[d_w - d_a] \tag{2}$$

$$B = T_a^2 - (A \times d_a) \tag{3}$$

T_w = observed period of oscillation for cell containing water,
T_a = observed period of oscillation for cell containing air,
d_w = density of water at test temperature, and
d_a = density of air at test temperature.

Alternatively, use the T and d values for the other reference liquid if one is used.

10.2.7 If the instrument is equipped to calculate density from the constants A and B and the observed T-value from the sample, then enter the constants in the instrument memory in accordance with the manufacturer's instructions.

10.2.8 Check the calibration and adjust if needed by performing the routine calibration check described in 10.3.

10.2.9 To calibrate the instrument to display relative density, that is, the density of the sample at a given temperature referred to the density of water at the same temperature, follow 10.2.1-10.2.7, but substitute 1.000 for d_w in performing the calculations described in 10.2.6.

10.3 Weekly calibration adjustments to constants A and B can be made if required, without repeating the calculation procedure.

NOTE 4—The need for a change in calibration is generally attributable to deposits in the sample tube that are not removed by the routine flushing procedure. Although this condition can be compensated for by adjusting A and B, it is good practice to clean the tube with warm chromic acid solution (**Warning**—Causes severe burns. A recognized carcinogen.) whenever a major adjustment is required. Chromic acid solution is the most effective cleaning agent; however, surfactant cleaning fluids have also been used successfully.

10.3.1 Flush and dry the sample tube as described in 10.2.1 and allow the display to reach a steady reading. If the display does not exhibit the correct density for air at the temperature of test, repeat the cleaning procedure or adjust the value of constant B commencing with the last decimal place until the correct density is displayed.

TABLE 1 Density of Water[A]

Temperature, °C	Density, g/mL	Temperature, °C	Density, g/mL	Temperature, °C	Density, g/mL
0.0	0.999840	21.0	0.997991	40.0	0.992212
3.0	0.999964	22.0	0.997769	45.0	0.990208
4.0	0.999972	23.0	0.997537	50.0	0.988030
5.0	0.999964	24.0	0.997295	55.0	0.985688
10.0	0.999699	25.0	0.997043	60.0	0.983191
15.0	0.999099	26.0	0.996782	65.0	0.980546
15.56	0.999012	27.0	0.996511	70.0	0.977759
16.0	0.998943	28.0	0.996231	75.0	0.974837
17.0	0.998774	29.0	0.995943	80.0	0.971785
18.0	0.998595	30.0	0.995645	85.0	0.968606
19.0	0.998404	35.0	0.994029	90.0	0.965305
20.0	0.998203	37.78	0.993042	100	0.958345

[A] Densities conforming to the International Temperature Scale 1990 (ITS 90) were extracted from Appendix G, *Standard Methods for Analysis of Petroleum and Related Products 1991*, Institute of Petroleum, London.

10.3.2 If adjustment to constant B was necessary in 10.3.1 then continue the recalibration by introducing redistilled, freshly boiled and cooled reagent water into the sample tube as described in 10.2.3 and allow the display to reach a steady reading. If the instrument has been calibrated to display the density, adjust the reading to the correct value for water at the test temperature (Table 1) by changing the value of constant A, commencing with the last decimal place. If the instrument has been calibrated to display the relative density, adjust the reading to the value 1.0000.

NOTE 5—In applying this weekly calibration procedure, it can be found that more than one value each for A and B, differing in the fourth decimal place, will yield the correct density reading for the density of air and water. The setting chosen would then be dependent upon whether it was approached from a higher or lower value. The setting selected by this method could have the effect of altering the fourth place of the reading obtained for a sample.

10.4 Some analyzer models are designed to display the measured period of oscillation only (T-values) and their calibration requires the determination of an instrument constant K, which must be used to calculate the density or relative density from the observed data.

10.4.1 Flush and dry the sample tube as described in 10.2.1 and allow the display to reach a steady reading. Record the T-value for air.

10.4.2 Introduce redistilled, freshly boiled and cooled reagent water into the sample tube as described in 10.2.3, allow the display to reach a steady reading and record the T-value for water.

10.4.3 Using the observed T-values and the reference values for water and air (10.2.4 and 10.2.5), calculate the instrument constant K using the following equations:

For density:

$$K_1 = [d_w - d_a]/[T_w^2 - T_a^2] \tag{4}$$

For relative density:

$$K_2 = [1.0000 - d_a]/[T_w^2 - T_a^2] \tag{5}$$

where:

T_w = observed period of oscillation for cell containing water,
T_a = observed period of oscillation for cell containing air,
d_w = density of water at test temperature, and
d_a = density of air at test temperature.

11. Procedure

11.1 Introduce a small amount (about 0.7 mL) of sample into the clean, dry sample tube of the instrument using a suitable syringe.

11.2 The sample can also be introduced by siphoning. Plug the external TFE-fluorocarbon capillary tube into the lower entry port of the sample tube. Immerse the other end of the capillary in the sample and apply suction to the upper entry port using a syringe or vacuum line until the sample tube is properly filled.

11.3 Turn on the illumination light and examine the sample tube carefully. Make sure that no bubbles are trapped in the tube, and that it is filled to just beyond the suspension point on the right-hand side. The sample must be homogeneous and free of even the smallest bubbles.

NOTE 6—If the sample is too dark in color to determine the absence of bubbles with certainty, the density cannot be measured within the stated precision limits of Section 14.

11.4 Turn the illumination light off immediately after sample introduction, because the heat generated can affect the measurement temperature.

11.5 After the instrument displays a steady reading to four significant figures for density and five for *T*-values, indicating that temperature equilibrium has been reached, record the density or *T*-value.

12. Calculation

12.1 *Calculating Density Analyzers*—The recorded value is the final result, expressed either as density in g/mL, kg/m^3 or as relative density. Note that kg/m^3 = 1000 × g/mL.

12.2 *Noncalculating Density Analyzers*—Using the observed *T*-value for the sample and the *T*-value for water and appropriate instrument constants determined in 10.4.3, calculate the density or relative density using Eq 6 and Eq 7. Carry out all calculations to six significant figures and round the final results to four.

For density:

$$\text{density, g/mL (kg/dm}^3\text{) at } t = d_w + K_1(T_s^2 - T_w^2) \qquad (6)$$

For relative density:

$$\text{relative density, } t/t = 1 + K_2(T_s^2 - T_w^2) \qquad (7)$$

where:

T_w = observed period of oscillation for cell containing water,
T_s = observed period of oscillation for cell containing sample,
d_w = density of water at test temperature,
K_1 = instrument constant for density,
K_2 = instrument constant for relative density, and
t = temperature of test,° C.

12.3 If it is necessary to convert a result obtained using the density meter to a density or relative density at another temperature, Guide D 1250 can be used only if the glass expansion factor has been excluded.

13. Report

13.1 In reporting density, give the test temperature and the units (for example: density at 20°C = 0.8765 g/mL or 876.5 kg/m^3).

13.2 In reporting relative density, give both the test temperature and the reference temperature, but no units (for example: relative density, 20/20°C = 0.xxxx).

13.3 Report the final result to the fourth decimal place.

14. Precision and Bias [8]

14.1 The precision of the method as obtained by statistical examination of interlaboratory test results at test temperatures of 15 and 20°C is as follows:

14.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following value only in one case in twenty:

Range	Repeatability
0.68–0.97 g/mL	0.0001

14.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Range	Reproducibility
0.68–0.97 g/mL	0.0005

14.2 *Bias*—After suggestions of its existence from literature[9], a study has been performed which has confirmed the presence of a bias between known density values for reference materials and from values determined according to this test method on the same reference materials. The matrix for this bias study comprised 15 participants, each analyzing four reference oils with certified density values, established by the Netherlands Meet Instituut (NMI), by pyknometry, covering densities in the range of 747 to 927 kg/m^3 at 20°C, with viscosities between 1 and 5 000 mPa.s (also at 20°C). This study is documented in ASTM Research Report RR-D02-1387. Method users should, therefore, be aware that results obtained by this test method can be biased by as much as 0.6 kg/m^3 (0.0006 g/mL).

15. Keywords

15.1 density; digital density analyzer; petroleum distillates; petroleum products; relative density

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[8] Statistical data is available as a research report from ASTM Headquarters. Request RR:D02-1387.

[9] Fitzgerald, H. and D., "An Assessment of Laboratory Density Meters," *Petroleum Review*, November 1992, pp. 544–549.

APPENDIX A-101

STANDARD TEST METHOD FOR KINEMATIC VISCOSITY OF TRANSPARENT AND OPAQUE LIQUIDS (THE CALCULATION OF DYNAMIC VISCOSITY)

Designation: D 445 – 97

An American National Standard
British Standard 2000: Part 71:1990

Designation: 71S1/97

Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)[1]

This standard is issued under the fixed designation D 445; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This test method has been approved by the sponsoring committee and accepted by the Cooperating Societies in accordance with established procedures.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method specifies a procedure for the determination of the kinematic viscosity, ν, of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity, η, can be obtained by multiplying the kinematic viscosity, ν, by the density, ρ, of the liquid.

NOTE 1—For the measurement of the kinematic viscosity and viscosity of bitumens, see also Test Methods D 2170 and D 2171.

1.2 The result obtained from this test method is dependent upon the behavior of the sample and is intended for application to liquids for which primarily the shear stress and shear rates are proportional (Newtonian flow behavior). If, however, the viscosity varies significantly with the rate of shear, different results may be obtained from viscometers of different capillary diameters. The procedure and precision values for residual fuel oils, which under some conditions exhibit non-Newtonian behavior, have been included.

1.3 The range of kinematic viscosities covered by this test method is from 0.2 to 300 000 mm^2/s (see Table A1.1) at all temperatures (see 6.3 and 6.4). The precision has only been determined for those materials, kinematic viscosity ranges and temperatures as shown in the footnotes to the precision section.

1.4 The values stated in SI units are to be regarded as the standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers[2]

D 1193 Specification for Reagent Water[3]

D 1217 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer[2]

D 1480 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer[2]

D 1481 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Lipkin Bicapillary Pycnometer[2]

D 2170 Test Method for Kinematic Viscosity of Asphalts (Bitumens)[4]

D 2171 Test Method for Viscosity of Asphalts by Vacuum Capillary Viscometer[4]

D 6074 Guide for Characterizing Hydrocarbon Lubricant Base Oils[5]

E 1 Specification for ASTM Thermometers[6]

E 77 Test Method for the Inspection and Verification of Thermometers[6]

2.2 *ISO Standards:*[7]

ISO Guide 25—General Requirements for the Calibration and Testing Laboratories

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.

Current edition approved Dec. 10, 1997. Published September 1998. Originally published as D 445 – 37T. Last previous edition D 445 – 96.

In the IP, this test method is under the jurisdiction of the Standardization Committee.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 04.03.

[5] *Annual Book of ASTM Standards*, Vol 05.03.

[6] *Annual Book of ASTM Standards*, Vol 14.03.

[7] Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

ISO 3104 Petroleum Products—Transparent and Opaque Liquids—Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity
ISO 3105 Glass Capillary Kinematic Viscometers—Specification and Operating Instructions
ISO 3696 Water for Analytical Laboratory Use—Specification and Test Methods
ISO 9000 Quality Management and Quality Assurance Standards—Guidelines for Selection and Use

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *density, n*—the mass per unit volume of a substance at a given temperature.

3.1.2 *dynamic viscosity, n*—the ratio between the applied shear stress and rate of shear of a liquid.

3.1.2.1 *Discussion*—It is sometimes called the coefficient of dynamic viscosity or, simply, viscosity. Thus dynamic viscosity is a measure of the resistance to flow or deformation of a liquid.

3.1.2.2 *Discussion*—The term dynamic viscosity can also be used in a different context to denote a frequency-dependent quantity in which shear stress and shear rate have a sinusodial time dependence.

3.1.3 *kinematic viscosity, n*—the resistance to flow of a fluid under gravity.

3.1.3.1 *Discussion*—For gravity flow under a given hydrostatic head, the pressure head of a liquid is proportional to its density, ρ. For any particular viscometer, the time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity, ν, where $\nu = \eta/\rho$, and η is the dynamic viscosity coefficient.

4. Summary of Test Method

4.1 The time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer.

5. Significance and Use

5.1 Many petroleum products, and some non-petroleum materials, are used as lubricants, and the correct operation of the equipment depends upon the appropriate viscosity of the liquid being used. In addition, the viscosity of many petroleum fuels is important for the estimation of optimum storage, handling, and operational conditions. Thus, the accurate determination of viscosity is essential to many product specifications.

6. Apparatus

6.1 *Viscometers*—Use only calibrated viscometers of the glass capillary type, capable of being used to determine kinematic viscosity within the limits of the precision given in the precision section.

6.1.1 Viscometers listed in Table A1.1, whose specifications meet those given in Specifications D 446 and in ISO 3105 meet these requirements. It is not intended to restrict this test method to the use of only those viscometers listed in Table A1.1. Annex A1 gives further guidance.

6.1.2 *Automation*—Automated viscometers, which have been shown to determine kinematic viscosity within the limits of precision given in Section 16 are acceptable alternatives. Apply a kinetic energy correction (see Specifications D 446 and ISO 3105) to kinematic viscosities less than 10 mm^2/s and flow times less than 200 s.

6.2 *Viscometer Holders*—Use viscometer holders to enable all viscometers which have the upper meniscus directly above the lower meniscus to be suspended vertically within 1° in all directions. Those viscometers whose upper meniscus is offset from directly above the lower meniscus shall be suspended vertically within 0.3° in all directions (see Specifications D 446 and ISO 3105).

6.2.1 Viscometers shall be mounted in the constant temperature bath in the same manner as when calibrated and stated on the certificate of calibration. See Specifications D 446, see Operating Instructions in Annex A1, Annex A2, and Annex A3. For those viscometers which have Tube L (see Specifications D 446) held vertical, vertical alignment shall be confirmed by using (*1*) a holder ensured to hold Tube L vertical, or (*2*) a bubble level mounted on a rod designed to fit into Tube L, or (*3*) a plumb line suspended from the center of Tube L, or (*4*) other internal means of support provided in the constant temperature bath.

6.3 *Temperature-Controlled Bath*—Use a transparent liquid bath of sufficient depth such, that at no time during the measurement of flow time, any portion of the sample in the viscometer is less than 20 mm below the surface of the bath liquid or less than 20 mm above the bottom of the bath.

6.3.1 *Temperature Control*—For each series of flow time measurements, the temperature control of the bath liquid shall be such that within the range from 15 to 100°C, the temperature of the bath medium does not vary by more than ±0.02°C of the selected temperature over the length of the viscometer, or between the position of each viscometer, or at the location of the thermometer. For temperatures outside this range, the deviation from the desired temperature must not exceed ± 0.05°C.

6.4 *Temperature Measuring Device in the Range from 0 to 100°C*—Use either calibrated liquid-in-glass thermometers (Annex A2) of an accuracy after correction of ±0.02°C or better, or any other thermometric device of equal or better accuracy.

6.4.1 If calibrated liquid-in-glass thermometers are used, the use of two thermometers is recommended. The two thermometers shall agree within 0.04°C.

6.4.2 Outside the range from 0 to 100°C, use either calibrated liquid-in-glass thermometers of an accuracy after correction of ± 0.05°C or better, or any other thermometric device of equal or better accuracy. When two temperature measuring devices are used in the same bath, they shall agree within ±0.1°C.

6.4.3 When using liquid-in-glass thermometers, such as those in Table A2.2, use a magnifying device to read the thermometer to the nearest ⅕ division (for example, 0.01°C or 0.02°F) to ensure that the required test temperature and temperature control capabilities are met (see 9.1). It is recommended that thermometer readings (and any corrections supplied on the certificates of calibrations for the thermometers) be recorded on a periodic basis to demonstrate compliance with the test method requirements. This information can be quite useful, especially when investigating issues or causes relating to testing accuracy and precision.

6.5 *Timing Device*—Use any timing device that is capable of taking readings with a discrimination of 0.1 s or better, and has an accuracy within ±0.07 % (see Annex A3) of the reading when tested over intervals of 200 and 900 s.

6.5.1 Electrical timing devices may be used if the current frequency is controlled to an accuracy of 0.05 % or better. Alternating currents, as provided by some public power systems, are intermittently rather than continuously controlled. When used to actuate electrical timing devices, such control can cause large errors in kinematic viscosity flow time measurements.

7. Reagents and Materials

7.1 *Chromic Acid Cleaning Solution*, or a nonchromium-containing, strongly oxidizing acid cleaning solution.

NOTE 2—**Warning:** Chromic acid is a health hazard. It is toxic, a recognized carcinogen, highly corrosive, and potentially hazardous in contact with organic materials. If used, wear a full face-shield and full-length protective clothing including suitable gloves. Avoid breathing vapor. Dispose of used chromic acid carefully as it remains hazardous. Nonchromium-containing, strongly oxidizing acid cleaning solutions are also highly corrosive and potentially hazardous in contact with organic materials, but do not contain chromium which has special disposal problems.

7.2 *Sample Solvent*, completely miscible with the sample. Filter before use.

7.2.1 For most samples a volatile petroleum spirit or naphtha is suitable. For residual fuels, a prewash with an aromatic solvent such as toluene or xylene may be necessary to remove asphaltenic material.

7.3 *Drying Solvent*, a volatile solvent miscible with the sample solvent (see 7.2) and water (see 7.4). Filter before use.

7.3.1 Acetone is suitable.

7.4 *Water*, deionized or distilled and conforming to Specification D 1193 or Grade 3 of ISO 3696. Filter before use.

8. Calibration and Verification

8.1 *Viscometers*—Use only calibrated viscometers, thermometers, and timers as described in Section 6.

8.2 *Certified Viscosity Reference Standards*[8] *(Table A1.2)*—These are for use as confirmatory checks on the procedure in the laboratory.

8.2.1 If the determined kinematic viscosity does not agree within ± 0.35 % of the certified value, recheck each step in the procedure, including thermometer and viscometer calibration, to locate the source of error. Annex A1 gives details of standards available.

8.2.2 The most common sources of error are caused by particles of dust lodged in the capillary bore and temperature measurement errors. It must be appreciated that a correct result obtained on a standard oil does not preclude the possibility of a counterbalancing combination of the possible sources of error.

8.3 The calibration constant, C, is dependent upon the gravitational acceleration at the place of calibration and this must, therefore, be supplied by the standardization laboratory together with the instrument constant. Where the acceleration of gravity, g, differs by more that 0.1 %, correct the calibration constant as follows:

$$C_2 = (g_2/g_1) \times C_1 \tag{1}$$

where the subscripts 1 and 2 indicate, respectively, the standardization laboratory and the testing laboratory.

9. General Procedure for Kinematic Viscosity

9.1 Adjust and maintain the viscometer bath at the required test temperature within the limits given in 6.3.1 taking account of the conditions given in Annex A2 and of the corrections supplied on the certificates of calibration for the thermometers.

9.1.1 Thermometers shall be held in an upright position under the same conditions of immersion as when calibrated.

9.1.2 In order to obtain the most reliable temperature measurement, it is recommended that two thermometers with valid calibration certificates be used (see 6.4).

9.1.3 They should be viewed with a lens assembly giving approximately five times magnification and be arranged to eliminate parallax errors.

9.2 Select a clean, dry, calibrated viscometer having a range covering the estimated kinematic viscosity (that is, a wide capillary for a very viscous liquid and a narrower capillary for a more fluid liquid). The flow time shall not be less than 200 s or the longer time noted in Specifications D 446.

9.2.1 The specific details of operation vary for the different types of viscometers listed in Table A1.1 The operating instructions for the different types of viscometers are given in Specifications D 446.

9.2.2 When the test temperature is below the dew point, affix loosely packed drying tubes to the open ends of the viscometer. The drying tubes must fit the design of the viscometer and not restrict the flow of the sample by pressures created in the instrument. Carefully flush the moist room air from the viscometer by applying vacuum to one of the drying tubes. Finally, before placing the viscometer in the bath, draw up the sample into the working capillary and timing bulb and allow to drain back as an additional safeguard against moisture condensing or freezing on the walls.

9.2.3 Viscometers used for silicone fluids, fluorocarbons, and other liquids which are difficult to remove by the use of a cleaning agent, shall be reserved for the exclusive use of those fluids except during their calibration. Subject such viscometers to calibration checks at frequent intervals. The solvent washings from these viscometers shall not be used for the cleaning of other viscometers.

10. Procedure for Transparent Liquids

10.1 Charge the viscometer in the manner dictated by the design of the instrument, this operation being in conformity

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[8] The ASTM Viscosity Oil Standards are available in 1-pt (0.47 L) containers. Purchase orders should be addressed to the Cannon Instrument Co., P.O. Box 16, State College, PA 16804. Shipment will be made as specified or by best means.

with that employed when the instrument was calibrated. If the sample contains solid particles, filter during charging through a (75-μm) filter (see Specifications D 446). If the sample is thought or known to contain fibers or solid particles, filter through a 75 μm screen, either prior to or during charging (see Specifications D 446).

NOTE 3—To minimize the potential of particles passing through the filter from aggregating, it is recommended that the time lapse between filtering and charging be kept to a minimum.

10.1.1 In general, the viscometers used for transparent liquids are of the type listed in Table A1.1, A and B.

10.1.2 With certain products which exhibit *gel-like* behavior, exercise care that flow time measurements are made at sufficiently high temperatures for such materials to flow freely, so that similar kinematic viscosity results are obtained in viscometers of different capillary diameters.

10.1.3 Allow the charged viscometer to remain in the bath long enough to reach the test temperature. Where one bath is used to accommodate several viscometers, never add or withdraw a viscometer while any other viscometer is in use for measuring a flow time.

10.1.4 Because this time will vary for different instruments, for different temperatures, and for different kinematic viscosities, establish a safe equilibrium time by trial.

10.1.4.1 Thirty minutes should be sufficient except for the highest kinematic viscosities.

10.1.5 Where the design of the viscometer requires it, adjust the volume of the sample to the mark after the sample has reached temperature equilibrium.

10.2 Use suction (if the sample contains no volatile constituents) or pressure to adjust the head level of the test sample to a position in the capillary arm of the instrument about 7 mm above the first timing mark, unless any other value is stated in the operating instructions for the viscometer. With the sample flowing freely, measure, in seconds to within 0.1 s, the time required for the meniscus to pass from the first to the second timing mark. If this flow time is less than the specified minimum (see 9.2), select a viscometer with a capillary of smaller diameter and repeat the operation.

10.2.1 Repeat the procedure described in 10.2 to make a second measurement of flow time. Record both measurements.

10.2.2 If the two determinations of kinematic viscosity, calculated from the flow time measurements, agree within the stated determinability figure (see 16.1) for the product, use the average of these determinations to calculate the kinematic viscosity result to be reported. Record the result. If the determinations of kinematic viscosity do not agree within the stated determinability, repeat the measurements of flow times after thorough cleaning and drying of the viscometers and filtering (where required, see 10.1) of the sample. If the material or temperature, or both, is not listed in 16.1, for temperatures between 15 and 100°C use as an estimate of the determinability 0.20 %, and 0.35 % for temperatures outside this range.

11. Procedure for Opaque Liquids

11.1 For steam-refined cylinder oils and black lubricating oils, proceed to 11.3 ensuring a thoroughly representative sample is used. The kinematic viscosity of residual fuel oils and similar waxy products can be affected by the previous thermal history and the following procedure described in 11.1.1-11.2.2 shall be followed to minimize this.

11.1.1 In general, the viscometers used for opaque liquids are of the reverse-flow type listed in Table A1.1, C.

11.1.2 Heat in the original container, in an oven, at 60 ± 2°C for 1 h.

11.1.3 Thoroughly stir the sample with a suitable rod of sufficient length to reach the bottom of the container. Continue stirring until there is no sludge or wax adhering to the rod.

11.1.4 Recap the container tightly and shake vigorously for 1 min to complete the mixing.

11.1.4.1 With samples of a very waxy nature or oils of high kinematic viscosity, it may be necessary to increase the heating temperature above 60°C to achieve proper mixing. The sample should be sufficiently fluid for ease of stirring and shaking.

11.2 Immediately after completing 11.1.4, pour sufficient sample to fill two viscometers into a 100-mL glass flask and loosely stopper.

11.2.1 Immerse the flask in a bath of boiling water for 30 min.

NOTE 4—**Precaution:** Exercise care as vigorous boil-over can occur when opaque liquids which contain high levels of water are heated to high temperatures.

11.2.2 Remove the flask from the bath, stopper tightly, and shake for 60 s.

11.3 Charge two viscometers in the manner dictated by the design of the instrument. For example, for the cross-arm or the BS U-tube viscometers for opaque liquids, filter the sample through a 75-μm filter into two viscometers previously placed in the bath. For samples subjected to heat treatment, use a preheated filter to prevent the sample coagulating during the filtration.

11.3.1 Viscometers which are charged before being inserted into the bath may need to be preheated in an oven prior to charging the sample. This is to ensure that the sample will not be cooled below test temperature.

11.3.2 After 10 min, adjust the volume of the sample (where the design of the viscometer requires) to coincide with the filling marks as in the viscometer specifications (see Specifications D 446).

11.3.3 Allow the charged viscometers enough time to reach the test temperature (see 11.3.1). Where one bath is used to accommodate several viscometers, never add or withdraw a viscometer while any other viscometer is in use for measuring flow time.

11.4 With the sample flowing freely, measure in seconds to within 0.1 s, the time required for the advancing ring of contact to pass from the first timing mark to the second. Record the measurement.

11.4.1 In the case of samples requiring heat treatment described in 11.1-11.2.1, complete the measurements of flow time within 1 h of completing 11.2.2. Record the measured flow times.

11.5 Calculate kinematic viscosity, ν, in mm ^{2}/s, from each measured flow time.

11.5.1 For residual fuel oils, if the two determinations of kinematic viscosity agree within the stated determinability figure (see 16.1), use the average of these determinations to calculate the kinematic viscosity result to be reported. Record the result. If the calculated kinematic viscosities do not agree, repeat the measurements of flow times after thorough cleaning and drying of the viscometers and filtering of the sample. If the material or temperature, or both, is not listed in 16.1, for temperatures between 15 and 100°C use as an estimate of the determinability 1.0 %, and 1.5 % for temperatures outside this range; it must be realized that these materials can be non-Newtonian, and can contain solids which can come out of solution as the flow time is being measured.

11.5.2 For other opaque liquids, no precision data is available.

12. Cleaning of Viscometer

12.1 Between successive determinations of kinematic viscosity, clean the viscometer thoroughly by several rinsings with the sample solvent, followed by the drying solvent (see 7.3). Dry the tube by passing a slow stream of filtered dry air through the viscometer for 2 min or until the last trace of solvent is removed.

12.2 Periodically clean the viscometer with the cleaning solution (**Warning**—see 7.1), for several hours to remove residual traces of organic deposits, rinse thoroughly with water (7.4) and drying solvent (see 7.3), and dry with filtered dry air or a vacuum line. Remove any inorganic deposits by hydrochloric acid treatment before the use of cleaning acid, particularly if the presence of barium salts is suspected.

NOTE 5—**Caution:** It is essential that alkaline cleaning solutions are not used as changes in the viscometer calibration can occur.

13. Calculation

13.1 Calculate the kinematic viscosity, ν, from the measured flow time, t, and the viscometer constant, C, by means of the following equation:

$$\nu = C \cdot t \tag{2}$$

where:

ν = kinematic viscosity, mm^2/s,

C = calibration constant of the viscometer, (mm^2/s)/s, and

t = mean flow time, s.

13.2 Calculate the dynamic viscosity, η, from the calculated kinematic viscosity, ν, and the density, ρ, by means of the following equation:

$$\eta = \nu \times \rho \times 10^{-3} \tag{3}$$

where:

η = dynamic viscosity, mPa·s,

ρ = density, kg/m^3, at the same temperature used for the determination of the kinematic viscosity, and

ν = kinematic viscosity, mm^2/s.

13.2.1 The density of the sample can be determined at the test temperature of the kinematic viscosity determination by an appropriate method such as Test Methods D 1217, D 1480, or D 1481.

14. Expression of Results

14.1 Report the test results for the kinematic or dynamic viscosity, or both, to four significant figures, together with the test temperature.

15. Report

15.1 Report the following information:

15.1.1 Type and identification of the product tested,

15.1.2 Reference to this test method or a corresponding international standard,

15.1.3 Result of the test (see Section 14),

15.1.4 Any deviation, by agreement or otherwise, from the procedure specified,

15.1.5 Date of the test, and

15.1.6 Name and address of the test laboratory.

16. Precision

16.1 *Determinability (d)*—The difference between successive determinations obtained by the same operator in the same laboratory using the same apparatus for a series of operations leading to a single result, would in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:[9,10,11,12,13,14,15,16]

Base oils at 40 and 100°C[9]	0.0020 y	(0.20 %)
Formulated oils at 40 and 100°C[10]	0.0013 y	(0.13 %)
Formulated oils at 150°C[11]	0.015 y	(1.5 %)
Petroleum wax at 100°C[12]	0.0080 y	(0.80 %)
Residual fuel oils at 80 and 100°C[13]	0.011 (y + 8)	
Residual fuel oils at 50°C[13]	0.017 y	(1.7 %)
Additives at 100°C[14]	$0.00106\ y^{1.1}$	
Gas oils at 40°C[15]	0.0013 (y+1)	
Jet fuels at –20°C[16]	0.0018 y	(0.18 %)

where: y is the average of determinations being compared.

16.2 *Repeatability (r)*—The difference between successive

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[9] These precision values were obtained by statistical examination of interlaboratory results from six mineral oils (base oils without additive package) in the range from 8 to 1005 mm^2/s at 40°C and from 2 to 43 mm ^{2}/s at 100°C, and were first published in 1989. Precision data available from ASTM Headquarters. Request RR:D02-1331 and RR:D02-1132. See Guide D 6074.

[10] These precision values were obtained by statistical examination of interlaboratory results from seven fully formulated engine oils in the range from 36 to 340 mm^2/s at 40°C and from 6 to 25 mm ^{2}/s at 100°C, and were first published in 1991. Precision data available from ASTM Headquarters. Request RR:D02-1332. See Guide D 6071.

[11] These precision values were obtained by statistical examination of interlaboratory results for eight fully formulated engine oils in the range from 7 to 19 mm ^{2}/s at 150°C, and first published in 1991. Precision data available from ASTM Headquarters. Request RR:D02-1333. See Guide D 6074.

[12] These precision values were obtained by statistical examination of interlaboratory results from five petroleum waxes in the range from 3 to 16 mm^2/s at 100°C, and were first published in 1988. Precision data available from ASTM Headquarters. Request RR:D02-1334.

[13] These precision values were obtained by statistical examination of interlaboratory results from fourteen residual fuel oils in the range from 30 to 1300 mm ^{2}/s at 50°C and from 5 to 170 mm^2/s at 80 and 100°C, and were first published in 1984. Precision data available from ASTM Headquarters. Request RR:D02-1198.

[14] These precision values were obtained by statistical examination of interlaboratory results from eight additives in the range from 145 to 1500 mm^2/s at 100°C and were first available in 1997. Precision data available from ASTM Headquarters. Request RR:D02-1421.

[15] These precision values were obtained by statistical examination of interlaboratory results from eight gas oils in the range from 1 to 13 mm^2/s at 40°C and were first available in 1997. Precision data available from ASTM Headquarters. Request RR:D02-1422.

[16] These precision values were obtained by statistical examination of interlaboratory results from nine jet fuels in the range from 4.3 to 5.6 mm ^{2}/s at– 20°C and were first available in 1997. Precision data available from ASTM Headquarters. Request RR:D02-1420.

results obtained by the same operator in the same laboratory with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:[9,10,11 ,12,13,14,15,16]

Base oils at 40 and 100°C[9]	0.0011 x	(0.11 %)
Formulated oils at 40 and 100°C[10]	0.0026 x	(0.26 %)
Formulated oils at 150°C[11]	0.0056 x	(0.56 %)
Petroleum wax at 100°C[12]	0.0141 $x^{1.2}$	
Residual fuel oils at 80 and 100°C[13]	0.013 $(x + 8)$	
Residual oils at 50°C[13]	0.015 x	(1.5 %)
Additives at 100°C[14]	0.00192 $x^{1.1}$	
Gas oils at 40°C[15]	0.0043 $(x+1)$	
Jet fuels at −20°C[16]	0.007 x	(0.7 %)

where: x is the average of results being compared.

16.3 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated below only in one case in twenty.[9 ,10,11,12,13,14 ,15,16]

Base oils at 40 and 100°C[9]	0.0065 x	(0.65 %)
Formulated oils at 40 and 100°C	0.0076 x	(0.76 %)
Formulated oils at 150°C[11]	0.018 x	(1.8 %)
Petroleum wax at 100°C[12]	0.0366 $x^{1.2}$	
Residual fuel oils at 80 and 100°C[13]	0.04 $(x + 8)$	
Residual oils at 50°C[13]	0.074 x	(7.4 %)
Additives at 100°C[14]	0.00862 $x^{1.1}$	
Gas oils at 40°C[15]	0.0082 $(x+1)$	
Jet fuels at −20°C[16]	0.019 x	(1.9 %)

where: x is the average of results being compared.

16.4 The precision for used oils has not been determined but is expected to be poorer than that for formulated oils. Because of the extreme variability of such used oils, it is not anticipated that the precision of used oils will be determined.

17. Keywords

17.1 dynamic viscosity; kinematic viscosity; viscometer; viscosity

ANNEXES

(Mandatory Information)

A1. VISCOMETER TYPES, CALIBRATION, AND VERIFICATION

A1.1 Viscometer Types

A1.1.1 Table A1.1 lists capillary viscometers commonly in use for viscosity determinations on petroleum products. For specifications and operating instructions, refer to Specifications D 446.

TABLE A1.1 Viscometer Types

Viscometer Identification	Kinematic Viscosity Range,[A] mm²/s
A. Ostwald Types for Transparent Liquids	
Cannon-Fenske routine[B]	0.5 to 20 000
Zeitfuchs	0.6 to 3 000
BS/U-tube[B]	0.9 to 10 000
BS/U/M miniature	0.2 to 100
SIL[B]	0.6 to 10 000
Cannon-Manning semi-micro	0.4 to 20 000
Pinkevitch[B]	0.6 to 17 000
B. Suspended-level Types for Transparent Liquids	
BS/IP/SL[B]	3.5 to 100 000
BS/IP/SL(S)[B]	1.05 to 10 000
BS/IP/MSL	0.6 to 3 000
Ubbelohde[B]	0.3 to 100 000
FitzSimons	0.6 to 1 200
Atlantic[B]	0.75 to 5 000
Cannon-Ubbelohde(A), Cannon Ubbelohde dilution[B](B)	0.5 to 100 000
Cannon-Ubbelohde semi-micro	0.4 to 20 000
C. Reverse-flow Types for Transparent and Opaque Liquids	
Cannon-Fenske opaque	0.4 to 20 000
Zeitfuchs cross-arm	0.6 to 100 000
BS/IP/RF U-tube reverse-flow	0.6 to 300 000
Lantz-Zeitfuchs type reverse-flow	60 to 100 000

[A] Each range quoted requires a series of viscometers. To avoid the necessity of making a kinetic energy correction, these viscometers are designed for a flow time in excess of 200 s except where noted in Specifications D 446.

[B] In each of these series, the minimum flow time for the viscometers with lowest constants exceeds 200 s.

A1.2 Calibration

A1.2.1 Calibrate working standard viscometers against master viscometers having a certificate of calibration traceable to a national standard. Viscometers used for analysis shall be calibrated in comparison with working standard viscometers or master viscometers, or by the procedures given in Specifications D 446 or ISO 3105. Viscometer constants shall be measured and expressed to the nearest 0.1 % of their value.

A1.3 Verification

A1.3.1 Viscometer constants shall either be verified by a similar procedure to A1.2, or conveniently checked by means of certified viscosity oils.

A1.3.2 These oils can be used for confirmatory checks on the procedure in a laboratory. If the measured viscosity does

TABLE A1.2 Viscosity Oil Standards[A]

Designation	Approximate Kinematic Viscosity, mm²/s					
	−40°C	20°C	25°C	40°C	50°C	100°C
S3	80	4.6	4.0	2.9	...	1.2
S6	...	11	8.9	5.7	...	1.8
S20	...	44	34	18	...	3.9
S60	...	170	120	54	...	7.2
S200	...	640	450	180	...	17
S600	...	2 400	1 600	520	280	32
S2 000	...	8 700	5 600	1 700	...	75
S8 000	...	37 000	23 000	6 700	...	...
S30 000	...	...	81 000	23 000	11 000	...

[A] The actual values for these standards are established and annually reaffirmed by cooperative tests. In 1991, tests were made using 15 different types of viscometers in 28 laboratories located in 14 countries.

[B] Kinematic viscosities may also be supplied at 100°F.

[C] Kinematic viscosities may also be supplied at 210°F.

not agree within ± 0.35 % of the certified value, recheck each step in the procedure including thermometer, timer, and viscometer calibration to locate the source of error. It should be appreciated that a correct result obtained on a certified oil does not preclude the possibility of a counterbalancing combination of the possible sources of error.

A1.3.2.1 A range of viscosity oil standards is commercially available, and each oil carries a certification of the measured value established by multiple testing. Table A1.2 gives the standard range of oils, together with the approximate viscosities over a range of temperatures.

A2. KINEMATIC VISCOSITY TEST THERMOMETERS

A2.1 Short-Range Specialized Thermometer

A2.1.1 Use a short-range specialized thermometer conforming to the generic specification given in Table A2.1 and Table A2.2 and to one of the designs shown in Fig. A2.1.

A2.1.2 The difference in the designs rests mainly in the position of the ice point scale. In Design A, the ice point is within the scale range, in Design B, the ice point is below the scale range, and in Design C, the ice point is above the scale range.

A2.2 Calibration

A2.2.1 Use liquid-in-glass thermometers with an accuracy after correction of 0.02°C or better, calibrated by a laboratory meeting the requirements of ISO 9000 or ISO 25, and carrying certificates confirming that the calibration is traceable to a national standard. As an alternative, use thermometric devices such as platinum resistance thermometers, of equal or better accuracy, with the same certification requirements.

A2.2.2 The scale correction of liquid-in-glass thermometers can change during storage and use, and therefore regular re-calibration is required. This is most conveniently achieved in a working laboratory by means of a re-calibration of the ice point, and all of the main scale corrections altered for the change seen in the ice point.

A2.2.2.1 It is recommended that the interval for ice-point checking be not greater than six months, but for new thermometers, monthly checking for the first six months is recommended. A complete new re-calibration of the thermometer, while permitted, is not necessary in order to meet the accuracy ascribed to this design thermometer until the ice-point change from the last full calibration amounts to one scale division, or more than five years have elapsed since the last full calibration.

TABLE A2.1 General Specification for Thermometers

NOTE 1—Table A2.2 gives a range of ASTM, IP, and ASTM/IP thermometers that comply with the specification in Table A2.1, together with their designated test temperatures. See Specification E 1 and Test Method E 77.

Immersion		Total
Scale marks:		
Subdivisions	°C	0.05
Long lines at each	°C	0.1 and 0.5
Numbers at each	°C	1
Maximum line width	mm	0.10
Scale error at test temperature, max	°C	0.1
Expansion chamber:		
Permit heating to	°C	105 up to 90, 120 between 90 and 95 130 between 95 and 105, 170 above 105
Total length	mm	300 to 310
Stem outside diameter	mm	6.0 to 8.0
Bulb length	mm	45 to 55
Bulb outside diameter	mm	no greater than stem
Length of scale range	mm	40 to 90

TABLE A2.2 Complying Thermometers

Thermometer No.	Test Temperature		Thermometer No.	Test Temperature	
	°C	°F		°C	°F
ASTM 132C, IP 102C	150		ASTM 128C, F/IP 33C	0	32
ASTM 110C, F/IP 93C	135	275	ASTM 72C, F/IP 67C	−17.8	0
ASTM 121C/IP 32C	98.9, 100	210, 212	ASTM 127C/IP 99C	−20	−4
			ASTM 126C, F/IP 71C	−26.1	−20
ASTM 129C, F/IP 36C	93.3	200	ASTM 73C, F/IP 68C	−40	−40
ASTM 48C, F/IP 90C	82.2	180	ASTM 74C, F/IP 69C	−53.9	−65
IP 100C	80				
ASTM 47C, F/IP 35C	60	140			
ASTM 29C, F/IP 34C	54.4	130			
ASTM 46C F/IP 66C	50	122			
ASTM 120C/IP 92C	40				
ASTM 28C, F/IP 31C	37.8	100			
ASTM 118C, F	30	86			
ASTM 45C, F/IP 30C	25	77			
ASTM 44C, F/IP 29C	20	68			

A2.2.2.2 Other thermometric devices, if used, will also require periodic recalibration. Keep records of all recalibration.

A2.2.3 *Procedure for Ice-point Re-calibration of Liquid-in-glass Thermometers.*

A2.2.3.1 Unless otherwise listed on the certificate of calibration, the re-calibration of calibrated kinematic viscosity thermometers requires that the ice-point reading shall be taken within 60 min after being at test temperature for not less than 3 min.

A2.2.3.2 Select clear pieces of ice, preferably made from distilled or pure water. Discard any cloudy or unsound portions. Rinse the ice with distilled water and shave or crush into small pieces, avoiding direct contact with the hands or any chemically unclean objects. Fill the Dewar vessel with the crushed ice and add sufficient water to form a slush, but not enough to float the ice. As the ice melts, drain off some of the water and add more crushed ice. Insert the thermometer, and pack the ice gently about the stem, to a depth approximately one scale division below the 0°C graduation.

A2.2.3.3 After at least 3 min have elapsed, tap the thermometer gently and repeatedly at right angles to its axis while making observations. Successive readings taken at least 1 min apart shall agree within 0.005°C.

A2.2.3.4 Record the ice-point readings and determine the thermometer correction at this temperature from the mean reading. If the correction is found to be higher or lower than

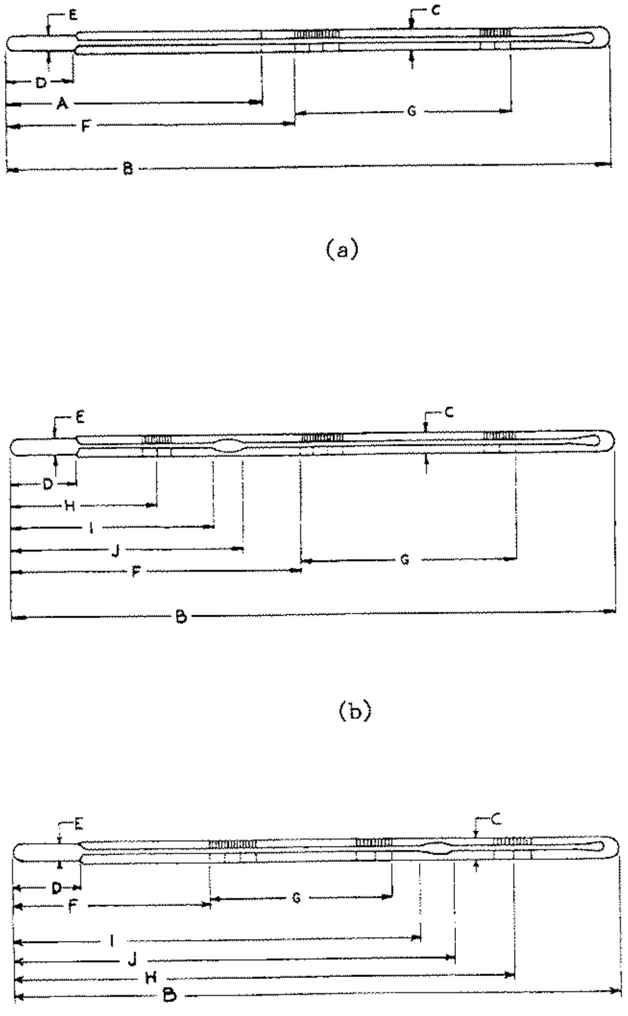

FIG. A2.1 Thermometer Designs

that corresponding to a previous calibration, change the correction at all other temperatures by the same value.

A2.2.3.5 During the procedure, apply the following conditions:

(*a*) The thermometer shall be supported vertically.

(*b*) View the thermometer with an optical aid that gives a magnification of approximately five and also eliminates parallax.

(*c*) Express the ice-point reading to the nearest 0.005°C.

A2.2.4 When in use, immerse the thermometric device to the same depth as when it was fully calibrated. For example, if a liquid-in-glass thermometer was calibrated at the normal total immersion condition, it shall be immersed to the top of the mercury column with the remainder of the stem and the expansion volume at the uppermost end exposed to room temperature and pressure. In practice, this means that the top of the mercury column shall be within a length equivalent to four scale divisions of the surface of the medium whose temperature is being measured.

A2.2.4.1 If this condition cannot be met, then an extra correction may be necessary.

A3. TIMER ACCURACY

A3.1 Regularly check timers for accuracy and maintain records of such checks.

A3.1.1 Time signals as broadcast by the National Institute of Standards and Technology are a convenient and primary standard reference for calibrating timing devices. The following can be used to an accuracy of 0.1 s:

WWV	Fort Collins, CO	2.5, 5, 10, 15, 20 MHz
WWVH	Kauai, HI	2.5, 5, 10, 15, MHz
CHU	Ottawa, Canada	3.33, 7.335, 14.67 MHz

A3.1.2 Radio broadcast of voice and audio on a telephone line at phone 303-499-7111. Additional time services are available from the National Institute of Standards and Technology.

APPENDIX A-102

METHOD VPH_MA
STANDARD OPERATING PROCEDURE FOR VOLATILE PETROLEUM HYDROCARBONS BY GAS CHROMATOGRAPHY

METHOD VPH_MA
STANDARD OPERATING PROCEDURE FOR VOLATILE PETROLEUM HYDROCARBONS-MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION BY GAS CHROMATOGRAPHY

Applicable Matrix or Matrices: Waters, Soils, and Sediments
Standard Compound List and Reporting Limits: See Appendix A

Approvals and Signatures

Laboratory Director: Christopher A. Ouellette Date: 8-8/00

QA Manager: Kim B. Watson Date: 8/8/00

Organic Technical Director: Bryce E. Stearns Date: 8/8/00

1.0 SCOPE AND APPLICATION

This method is used to determine the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil samples. Volatile aliphatic hydrocarbons are collectively quantitated within two ranges: C5 through C8 and C9 through C12. Volatile aromatic hydrocarbons are collectively quantitated within the C9 to C10 range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36° C and 220°C. Individual concentrations of benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and methyl-tert-butylether (MTBE) are also quantitated using this method. This method is based on a purge-and-trap, gas chromatography (GC) procedure using in-series Photoionization and Flame Ionization Detectors (PID/FID). Like all GC procedures, this method is subject to a "false positive" bias in reporting of Target Analytes, in that non-targeted hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated as Target Analyte. Confirmatory analysis by a GC/MS procedure or other suitable method is recommended in cases where a Target Analyte reported by this method exceeds an applicable reporting or clean up standards, and /or where co-elution of a non-targeted hydrocarbon compound is suspected.

2.0 SUMMARY OF METHOD

2.1 This method provides the sample preparation and GC conditions that will be applied to analyze volatile aliphatic and aromatic hydrocarbons based on the method prepared by the Massachusetts Department of Environmental Protection (MADEP). Reporting limits are presented in Section 19.0

2.2 Samples are analyzed using a purge and trap system connected to a GC equipped with a PID and FID in series. Quantitation is based on comparing the PID and FID detector response of a sample to a standard comprised of aromatic and aliphatic hydrocarbons. The GC is calibrated using five standard concentrations.

2.3 The PID is used to measure the individual concentrations of targeted analytes (BTEX/MTBE/naphthalene) and collective concentrations of C_9 through C_{10} aromatic hydrocarbons. The FID is used to measure the collective concentrations of aliphatic hydrocarbons within the C_5 through C_8 and C_9 through C_{12} ranges.

2.4 This method is suitable for the analysis of waters, soils, and sediments. Water samples may be analyzed directly for volatile petroleum hydrocarbons by purge and trap concentration and GC. Soil samples are dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanol solution is then analyzed by purge and trap GC.

3.0 DEFINITIONS

3.1 Analytical Batch is defined as a group of field samples with similar matrices that are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.2 Calibration Check Standard is defined as a calibration standard used to periodically check the calibration state of the instrument. The calibration check standard is prepared from the same stock solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.3 Calibration Standard is defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

3.4 C_5 through C_8 Aliphatic Hydrocarbons are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram from n-pentane (C_5) to just before n-nonane (C_9).

3.5 C_9 through C_{12} Aliphatic Hydrocarbons are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram from n-nonane (C_9) to just before naphthalene.

3.6 C_9 through C_{10} Aliphatic Hydrocarbons are defined as all aliphatic hydrocarbon compounds which elute on the PID chromatogram from just after o-xylene to just before naphthalene. Although it is an aromatic compound with 10 carbon atoms, naphthalene is excluded from this range because it is evaluated as a separate (Target) analyte.

3.7 Field Duplicates are defined as two separate samples collected at the same time and place under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.8 Laboratory Fortified Blank (LFB) or Laboratory Control Sample (LCS) is defined as a reagent water blank or clean sand blank fortified with a matrix spiking solution.

3.9 Laboratory Duplicates are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of the laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage.

3.10 Laboratory Fortified Matrix (LFM) or Matrix Spike (MS) Sample is defined as an environmental sample that has been spiked with a matrix spiking solution containing known concentrations of method analytes. The LFM sample is treated and analyzed exactly as a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the LFM sample corrected for background concentrations.

3.11 Laboratory Method Blank (VBLK##) is defined as an aliquot of reagent water or clean sand spiked with a surrogate standard. The laboratory method blank is treated exactly as a sample, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.12 Matrix Spiking Solution is defined as a solution prepared independently from the calibration standards, containing known concentrations of method analytes.

3.13 System Solvent Blank or Instrument Blank is defined as an aliquot of method solvent (e.g., methanol or deionized water) that is directly purged into the GC system. The purpose of the Solvent Blank is to determine the level of noise and baseline rise attributable solely to the GC system, in the absence of any other analytes or contaminates.

3.14 Target VPH Analytes are defined as benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, naphthalene, and methyl-tert-butylether.

3.15 Unjustified C_5 through C_8 Aliphatic Hydrocarbons are defined as all hydrocarbon compounds which elute on the FID chromatogram from n-pentane (C_5) to just before n-nonane (C_9).

3.16 Unjustified C_9 through C_{12} Aliphatic Hydrocarbons are defined as all hydrocarbon compounds which elute on the FID chromatogram from n-nonane (C_9) to just before naphthalene.

3.17 Volatile Petroleum Hydrocarbons (VPH) are defined as collective fractions of hydrocarbon compounds eluting from n-pentane to naphthalene, excluding Target VPH Analytes. VPH is comprised of C_5 through C_8 Aliphatic Hydrocarbons, C_9 through C_{12} Aliphatic Hydrocarbons, and C_9 through C_{10} Aromatic Hydrocarbons.

3.18 Volatile Petroleum Hydrocarbons (VPH) Component Standard is defined as a 13 component mixture of the aliphatic and aromatic compounds listed in Table 1. The compounds comprising the VPH Component Standard are used to (a) define the individual retention times and chromatographic response factors for each of the Target VPH Analytes, (b) define and establish the windows for collective aliphatic and aromatic hydrocarbon ranges of interest, and (c) determine average chromatographic response factors that can in turn be used to calculate the collective concentration of hydrocarbons within these ranges.

3.19 All other terms are as defined in SW-846, "Test Methods for Evaluating Solid Waste", USEPA, September, 1986, and as amended and updated.

4.0 INTERFERENCES

4.1 Samples may become contaminated by the diffusion of volatile organics through the vial septum. Methanol and water trip blanks should be analyzed to check for such contamination.

4.2 Whenever high level and low level samples are analyzed sequentially, contamination may occur. To avoid contamination, thorough cleaning of the syringe and purge vessels in addition to the analysis of cleaning blanks is necessary.

4.3 Certain compounds such as chlorinated solvents, ketones, and ethers will be quantitated as volatile petroleum hydrocarbons. Additional sample clean-up or confirmation analysis may be required.

4.4 All peaks eluting after 1,2,4-trimethylbenzene on the PID chromatogram are quantitated as aromatic hydrocarbons. Since some of these peaks might be aliphatic compounds, this method may overestimate the actual aromatic hydrocarbons present.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 STL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in these methods. Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. STL also has a written environmental health and safety plan.

5.3 Please note chemicals that have the potential to be highly toxic or hazardous, the appropriate MSDS must be reviewed by the employee before handling the chemical.

6.0 EQUIPMENT AND SUPPLIES

6.1 Gas chromatograph: analytical systems equipped with a photoionization detector (PID) and flame ionization detector (FID) are used in series to detect the analytes.

6.2 Purge and Trap Unit: Dynatec PTA-30WS or Tekmar 2050 auto sampler connected to an LSC-2000 or equivalent.

6.3 Data system: Fision's Vax based Multi-Chrom Version 2.11 or equivalent (TARGET).

6.4 Fused Silica Capillary Column: RTx-502.2 (105m X 0.53 mm ID, 3.0 µm film thickness or equivalent.

6.5 Syringes: 5 mL Luerlock glass hypodermic and 5 mL gas-tight syringe with shutoff valve

7.0 REAGENTS AND STANDARDS

7.1 Reagents/Solvents

7.1.1 Purge and Trap grade methanol: The methanol must not contain analytes of interest above the quantitation limit for 100 µL of methanol.

7.1.2 Reagent water: The reagent water is RO boiled and stored in glass amber 1 liter bottles until use. Analytes of interest must be below the quantitation limit. This can be checked by using an instrument blank analysis.

7.2 Standards - Formulation of standards is located in the Standards Formulation Notebook under Method MAVPH. Standards must be made up monthly and stored in the freezer at 0-10 °C.

Table 1: Curve and LCS Concentrations

Compound	LCS (µg/L)	MA-Mix (µg/L)				
		Mix A	Mix B	Mix C	Mix D	Mix E
Pentane	40	10	20	40	80	160
2-methylpentane	60	15	30	60	120	240
Methyl-t-butylether	60	15	30	60	120	240
2,2,4-trimethylpentane	60	15	30	60	120	240
Benzene	20	5	10	20	40	80
Toluene	60	15	30	60	120	240
Nonane	40	10	20	40	80	160
Ethylbenzene	20	5	10	20	40	80
m & p-xylene	80	20	40	80	160	320
o-xylene	40	10	20	40	80	160
1,2,4-trimethylbenzene	40	10	20	40	80	160
Naphthalene	40	10	20	40	80	160
2,5-dibromotoluene (ss)		10	20	40	80	160

To calculate the ranges, the summation of the peak areas is plotted against the total mass injected. Table 2 is a listing of the collective concentrations within each hydrocarbon range.

Table 2: Concentrations within Each Hydrocarbon Range

Component	Concentration (µg/L)				
	Mix A	Mix B	Mix C	Mix D	Mix E
$C_5 - C_8$	40	80	160	320	640
$C_9 - C_{12}$	10	20	40	80	160
$C_9 - C_{10}$	20	40	80	160	320

7.3 Determination of VPH Aromatic and Aliphatic Ranges: Non-target analytes are analyzed with the VPH calibration. These compounds are used for quantitation of VPH Aromatic and Aliphatic ranges.

7.3.1 Using the FID chromatogram, calculate a collective RF, CF, or LR for the total mass concentration of the $C_5 - C_8$ Aliphatic Hydrocarbons. Tabulate the collective peak area response of the three compounds (n-pentane, 2-methylpentane, 2,2,4-trimethylpentane) against the collective mass injection.

7.3.2 Using the FID chromatogram, calculate a collective RF, CF, or LR for the total mass concentration of the $C_9 - C_{12}$. This value is the value for n-nonane, the only aliphatic standard within this range.

7.3.3 Using the PID chromatogram, calculate a collective RF, CF, or LR for the total mass concentration of the $C_9 - C_{10}$. This value is the value for 1,2,4-trimethylbenzene, the only aromatic standard within this range.

7.4 The VPH Aromatic and Aliphatic ranges are set up using the following marker compounds in Table 3.

Table 3: VPH Marker Compounds

Hydrocarbon Range	Beginning Marker	Ending Marker
$C_5 - C_8$ Aliphatic Hydrocarbons (FID)	0.1 min before n-pentane	0.01 min before n-nonane
$C_9 - C_{12}$ Aliphatic Hydrocarbons (FID)	0.01 min before n-nonane	0.1 min before naphthalene
$C_9 - C_{10}$ Aromatic Hydrocarbons (PID)	0.1 min after 0-xylene	0.1 min before naphthalene

Note: The retention time for dodecane (12) is approximately 2 minutes less than the retention time for naphthalene, using the column and chromatographic conditions recommended for this method. For simplicity, naphthalene is used as the marker for the $C_9 - C_{12}$ Aliphatic Hydrocarbon range.

7.5 Surrogate Standard: The analyst must monitor both the performance of the analytical system and the effectiveness of the method with sample matrices by spiking each sample, blank, and matrix spike with a surrogate standard. The surrogate standard is also added to the VPH calibration standard solutions. The recommended surrogate standard is 2,5-dibromotoluene, which elutes after all aliphatic and aromatic compounds of interest. The use of another compound is permissible.

7.5.1 Surrogate Spiking Solution: From a stock standard solution prepared as in Section 7.2, prepare a surrogate spiking solution at 50 µg/mL in methanol. Add 4.0 µL of this surrogate spiking solution directly into the 5 mL syringe with every aqueous sample, blank, and matrix spike. 1.0 mL of the surrogate spiking solution is added to soil samples during the extraction step (Section 11.0) . The use of higher concentrations are permissible, and may be advisable when spiking highly contaminated samples.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Aqueous Samples:

8.1.1 A minimum of three 40 mL vials must be collected for water samples. Samples must be acidified to a pH of 2.0 or less at the time of collection.

8.1.2 A chain of custody form must accompany all sample vials and must document the date and time of sample collection and acid preservation. The pH of all water samples must be determined by the laboratory unless sample vials containing acid for field preservation were supplied by the laboratory (this must be noted on the chain of custody). The pH measurement may be performed on left over sample. Any sample found to contain a pH above two must be so noted on the laboratory/data report sheet.

8.1.3 A reagent water trip blank should accompany each batch of water samples.

8.1.4 Any sample received by the laboratory that is not packed in ice or cooled to 4 °C must be so noted on the laboratory/data report sheet.

8.1.5 Aqueous samples must be analyzed within 14 days of collection. If the pH of the sample is > 2, the samples must be analyzed within 7 days of collection.

8.2 Soil Samples:

8.2.1 Soil samples must be collected in a manner that minimizes sample handling and agitation. The use of specially designed air-tight collection samplers or a 30 mL plastic syringe with the end sliced off is recommended. All sediment must be cooled to 4°C immediately after collection.

8.2.2 **Methanol preservation of soil samples is mandatory**. Methanol (purge and trap grade) must be added to the sample vial before or immediately after sample collection. In lieu of the in-field preservation of samples with methanol, soil samples may be obtained in specially designed air-tight sample devices, if the samples are extruded and preserved in methanol within 48 hours of collection.

8.2.3 The desired ratio of the methanol-to-soil is 1 mL methanol/1 gram soil, ± 25%. The exact weight of the soil sample and volume of methanol must be known or ascertained by the laboratory when calculating and reporting soil concentration data. This requires an estimate on the density and moisture content of the soil sample; a good estimate for most soils is 8-10 mL of displaced volume for 15 grams of soil. **In all cases, the soil sample in the vial must be completely covered by methanol.**

8.2.4 **Samples** for VPH analysis should be collected in duplicate or 40 mL vials. An additional sample of the soil must also be obtained (without methanol) to allow for a determination of soil moisture content and VPH dry weight correction factors.

8.2.5 A methanol trip blank should accompany each batch of samples.

8.2.6 A chain of custody form must accompany all sampling vials and must document the date and time of sample collection and, where appropriate, the volume of methanol added. Observations of vial leakage must be so noted on the laboratory/data report sheet.

8.2.7 Soil samples must be analyzed within 28 days of collection.

8.3 A summary of sample collection, preservation, and holding times is provided in Table 4.

Table 4: Holding Times and Preservatives for VPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	40 mL VOC vials w/Teflon-lined septa screw caps	Add 3 to 4 drops of 1:1 HCl; cool to 4°C	14 days

Soil/Sediment Samples	VOC vials w/Teflon-lined septa screw caps 40 mL vials: add 15 g soil	1 mL methanol for every g soil; add before or at time of sampling; cool to 4°C	28 days

9.0 QUALITY CONTROL

9.1 Quality Control Standard (LCS): A quality control sample from a second source is run directly after the curve and analyzed at the mid point MA_MIX C. The acceptance criteria is obtained from the MADEP_VPH method and is provided in Table 5.

Table 5: LCS and MS/MSD Acceptance Criteria

Parameter	Water and Soil LCS/MS/MSD % Recovery	Water and Soil LCS/MS/MSD RPD (%)
Pentane	70 - 130	50
2-methylpentane	70 - 130	50
Methyl-t-butylether	70 - 130	50
2,2,4-trimethylpentane	70 - 130	50
benzene	70 - 130	50
toluene	70 - 130	50
nonane	70 - 130	50
ethylhexzene	70 - 130	50
m/p xylene	70 - 130	50
o-xylene	70 - 130	50
naphthalene	70 - 130	50
2,5 dibromotoluene (surrogate)	70 - 130	50

9.2 Instrument Blank: One per analytical window with the first one analyzed directly after the MA Mix E in the curve. Subsequent instrument blanks are to be analyzed after continuing check standards and after highly contaminated samples to demonstrate that there is no carryover into samples. Instrument blanks are to be sequentially labeled throughout the analytical run (VIBLKA1, VIBLAK2, etc.). All analytes must be less than the QL (MA-Mix A) to continue analysis.

9.3 Method Blank: One per analytical window with the first one analyzed directly after the first instrument blank. Method blanks are sequentially labeled throughout the analytical run (VBLKA1, VBLKA2, etc.). All analytes must be less than the reporting limit (MA-Mix A) to continue analysis. The water method blank consists of 5.0 mLs of reagent water. The soil method blank consists of 15 g cleaned pool sand in 5 mL of reagent grade methanol fortified with 1.0 mL of VPH surrogate. 100 µL of this extract is added to 5 mL of reagent water.

9.4 Surrogate Standards: Injected into all blanks and samples prior to analysis.

$$Surrogate\ Recovery\ (\%) = \frac{SR}{SA} * 100$$

Where:
SR = Spike Result
SA = Spike Added (concentration)

9.5 Matrix Spike/Matrix Spike Duplicate: An MS/MSD analysis is required every 20 samples per matrix. The MS/MSD analysis consists of spiking two aliquots of the same sample with a known concentration of all compounds on the Target Compound List. Matrix spike/matrix spike duplicate recovery limits are listed in Table 2. Individual component recoveries are calculated with the following equation:

$$MS\ Recovery\ (\%) = ((SSR\text{-}SR)/SA))*100$$

SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

The Relative Percent Difference (%RPD) between matrix spike and matrix spike duplicate analysis is calculated with the following equation:

$$\%\ RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

Where:
RPD = Relative Percent Difference
D_1 = First Sample Value
D_2 = Second Sample Value (duplicate)

9.6 Laboratory Control Sample (LCS). The LCS analysis consists of spiking either 5.0 mLs of reverse osmosis water with a known concentration of all compounds on the target compound list, as well as the surrogate compounds.

9.7 The MS/MSD and LCS are reviewed together. If compounds are failing in the MS/MSD and acceptable in the LCS the outages will assume to be matrix related. If outages exist in the LCS the entire batch must be reviewed with corrective action followed. Corrective action may include reanalysis of the batch.

9.8 Table 6 provides quality control criteria and corrective action procedures

Table 6: Quality Control and Corrective Action

Method VPH_MA			
Quality Control Criteria	**Frequency**	**Acceptance**	**Corrective Action**
5 point initial calibration (ICAL): MA Mix A, B, C, D, and E	As Required	Correlation coefficient $\geq$ 0.99 $R^2 = 0.98$	Recalibrate, mix new standards, reanalyze
CCAL MA Mix C	Every 10 samples	± 25%	Re-shoot, check integrations, mix new std. Reanalyze ICAL
Method Blank	After Each CCAL	Targets < Reporting Limit	Reanalyze, check for contamination, correct as required
Samples	--	Concentrations below highest calibration standard (MA Mix E For target Aromatic analytes	Dilute and reanalyze samples that are more concentrated than the highest calibration standard (MA Mix E)
Surrogates	Every sample, blank and QC sample must be spiked	See control limits in SOP	Any sample with outages must be reanalyzed to

	with surrogate		confirm. Present both sets of data.
Matrix Spike/Matrix Spike Duplicate	1 set every 20 samples, Full compound list spike required	Comparable results for spike and duplicate %RPD ± 50%	Evaluate LCS. If compounds failing in MS/MSD are acceptable in the LCS the outages will assume to be matrix related. Use professional judgement
LCS or ICV (at Mix C level) [second source]	Once per 20 samples (full compound list; independent std)	See control limits in table 2 of the SOP	Check Std., Check Quantitation, Evaluate MS/MSD. Reanalyze batch if failing compounds are present in the samples.

9.8 The procedure recommended in SW-846 for the determination of retention time windows is as follows:

- Make three injections of all single component standard mixtures and multi-response products (i.e. PCBs) throughout the course of a 72 hour period. Calculate the standard deviation of the three absolute retention times for each single component standard. For multi-response products, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples. The retention time window is defined as ± 3 times the standard deviation of the absolute retention times for each standard. The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed.

9.9 It is the laboratories experience that the SW-846 procedure results in retention time windows that are very tight and that favor false negatives. This would result in analytes that are present in the sample to not be reported. SW-846 is a guidance document that encourages modifications based on laboratory expertise. For this reason, the laboratory has taken a more conservative approach to the establishment of retention time windows.

9.10 Each analytical sequence is thoroughly reviewed and a retention time of ± 0.08 minutes from the mid-point standard is used for identification purposes. In addition, the laboratory will look at the retention time shift of the surrogates in each sample to see if further compensation of the retention time window is necessary. This routine, while more time consuming than the SW-846 approach prevents the laboratory from reporting false negatives.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Initial Calibration - Prior to sample analysis a five point calibration curve is analyzed followed by a quality control sample (LCS). A typical analytical sequence is as follows in Table 7:

Table 7: Analytical Sequence

Analysis	Lab ID
1	MA Mix A
2	MA Mix B
3	MA Mix C
4	MA Mix D
5	MA Mix E
6	VIBLK
7	LCS (at mid level)
8	VBLK##
9-18	10 Samples
19	MA-Mix C
20	LCS
21	VBLK##
22-31	10 Samples
32	VSTD MA-Mix C

$$\% \ RSD = \frac{SD}{x} * 100$$

10.2 The initial calibration must meet the following controls:

Where:

SD = Standard deviation of initial relative response factors (per

compound)
x = Mean of initial relative response factors (per compound)

For quantitation, the correlation coefficient (r) must be $\geq$0.99 (MA-DEP criteria)using a linear regression ($r^2 \geq$0.98), or if average response factor is used $\leq$20%RSD. A percent relative standard deviation (%RSD) is calculated for each compound with the following equation:

10.3 Continuing Calibration - As indicated in the analytical sequence instrument stability is verified every 10 sample injections. The 20 ppb standard is used for verification, and must pass for opening and closing an analytical window.

10.4 A check standard must be analyzed every 10 sample injections. In order to continue the analysis, the check standards must meet the following criteria:

10.4.1 The calculated values in the opening and closing check standard must fall within ± 25% difference of the minimal amount.

$$\% \text{ Difference} = \frac{(\text{calculated - nominal})}{\text{nominal}} * 100$$

10.4.2 Retention times must fall within ± 0.08 minutes of the calibration curve.

10.5 If these quality control criteria are not met, standards may be re-injected a second time. If they still fail, GC maintenance may be performed and recalibration is required.

10.6 When the sample analysis is completed, the analytical sequence must end with a passing closing standard.

10.7 For analytical windows containing medium level soil samples the check standards will contain 100 µL of methanol per 5 mL of water to show the effects of purging with methanol on analytes.

11.0 PROCEDURE

11.1 Water Samples – Introduce volatile compounds into a GC using a purge-and – trap concentrator.

11.1.1 Manual Injection:

- Remove plunger from 5 mL syringe and attach a closed syringe value. Open sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only on 40 mL vial, the analyst should fill the second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20 mL syringe would allow the use of only one syringe. If a second analysis is needed, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

- If necessary, based on screen results, samples should be diluted prior to injection into the purge chamber. In such cases, all steps must be performed without delay until the diluted sample is in a gas-tight syringe.

- Dilutions are made directly in the 43 mL vial. Record the dilution in the logbook.

- Fill a 5 mL syringe with diluted sample as in paragraph 11.1.1.

- Add 4.0 µL of the surrogate spiking solution through the valve bore of the syringe. Close the valves.

- Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe values and inject the sample into the purging chamber.

- Close both valves and purge the sample for 11 minutes. Purge and trap conditions are shown in Table 9.

Table 9: Purge and Trap Conditions

Purge Flow:	40 mL/min
Purge Time:	11 minutes
Dry Purge:	1 minute
Desorb Temperature:	250°C

Desorb Time:	4 minutes
Bake Time:	7 minutes
Bake Temperature:	260°C

- At the conclusion of the purge time, attach the trap to the chromatograph (if necessary), adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 260°C and backflushing the trap with inert gas between 15 and 20 mL/min for 4 minutes.

- While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

- After desorbing the sample, recondition the trap by returning the purge-and-trap device to purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin flow through the trap. The trap temperature should be maintained at 260°C. After approximately 7 to 15 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. After a highly concentrated sample, a longer baking time may be necessary. When cool, the trap is ready for the next sample.

11.1.2 Autosampler:

- Prepare sample in 43 mL vials for analysis. Allow samples to come to ambient temperature.

- Samples, LCSs, and blanks are spiked with 33.6 µL of 50 mL 1,2-dibromotoluene directly into the 43 mL vial.

- If necessary, based on screen results, samples should be diluted prior to injection into the purge chamber. In such cases, all steps must be performed without delay until the diluted sample is in a gas-tight syringe.

- Dilutions are made directly in a 43 mL vial. Record the dilution in the logbook.

- Place samples on autosampler tray.
- Choose "Program Setup" on instrument screen. Press "Auto" to begin.
- 5 mL aliquot of sample is transferred to the purging vessel and purged for 11 minutes. Purge and trap conditions are shown in Table 9.

11.1.3 If the concentration of an analyte or hydrocarbon fraction in a sample exceeds the calibration range, a dilution of the sample is required. If a sample analysis results in a saturated detector response for a compound, the analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of the interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

11.1.4 All dilutions should keep the detector response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

11.2 Soil and Sediment Samples: (extracted with methanol) – An aliquot of the extract is added to reagent water and introduced into the gas chromatograph using purge-and-trap concentrator.

11.2.1 If the soil sample received has not been extracted, then 15 g of sample is extracted in 15 mL of methanol. The analyst will record tare weight of the vial, final weight of the vial plus soil sample, and volume of methanol used for extraction.

11.2.2 If the soil samples are to be analyzed undiluted, 860 µL of methanol extract is added to 43 mL of R.O. water. The sample is then loaded onto the autosampler

11.2.3 Add 600 µL of 50 ppm 1,2-dibromotoluene (surrogate spike) directly into the 43 mL vial of all samples. The concentration and/or the volume of the surrogate spiking compound may need to be increased for samples that are highly contaminated (based on screening and/or visual/olfactory evidence), to prevent dilution to below detectable limits. Shake all samples for two minutes and sonicate for 20 minutes.

11.2.4 Allow sediment to settle until a layer of methanol is apparent.

11.2.5 Using a microliter syringe, withdraw an appropriate aliquot of the methanol extract for sparging. Sample screening data can be used to determine the volume of methanol extract to add to the 43 mL of reagent water for analysis. All dilutions must keep the response of the major constituents in the upper half of the linear range of the calibration curve.

11.2.6 Place 43 mL vials on autosampler

11.2.7 The autosampler pulls 5 mL aliquots from the 43 mL vials to transfer to the purging vessel. Purge and trap conditions are shown in Table 9.

11.2.8 Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

11.2.9 If the response exceeds the calibration or linear range for VPH Target analytes, a smaller aliquot of methanol or aqueous sample is used.

11.3 GC configuration: The purge and trap unit transfer line is directly connected to the analytical column.

Table 8: GC Condition

Initial Temperature:	45°C
Initial Time:	0 minutes
Rate #1:	3°/minutes
Temperature:	90°C
Hold:	0 minuets
Rate #2:	5°/minutes
Temperature:	140°C
Hold:	0 minutes
Rate #3:	45°/minutes
Temperature:	230°C
Hold:	8 minutes
Carrier Gas Flow:	15 mL/min
FID make-up:	15 mL/min
FID hydrogen:	30 psi
FID air:	300 psi

12.0 CALCULATIONS

12.1 Quantitation: A linear curve is used for quantitation of analytes:

$$y = a_o + (1/a_1) * x$$

Where:
y = concentration
x = peak height or area
a_o = intercept
$(1/a_1)$ = slope

12.2 From injected sample extract concentration the sample concentrations are calculated as follows:

Water Samples:

$$C_x\,(ug/L) = conc.\ purged\ (ug/L) * DF$$

DF= Dilution Factor

Soil Samples:

$$C_x\,(ug/Kg\ dry\ weight) = conc.\ purged\ (ug/L) * \frac{purge\ volume\,(L)}{spl.\ amount\ (Kg)} * \frac{100}{\%\ solids} * DF$$

DF= Dilution Factor

12.3 The following quantitation rules apply for reporting

12.3.1 By definition, the collective concentrations of Aliphatic and Aromatic fractions of interest **exclude** the individual concentrations of VPH Target Analytes. Accordingly, a series of data manipulation steps are necessary to adjust the collective range to eliminate “double counting” of analytes.

12.3.2 The necessary data manipulation steps may be taken by the laboratory reporting the range concentration data, or by the data user. The extent of data manipulations taken by the laboratory must be noted on the data report form.

12.3.3 Subtract the concentration of the surrogate compound(s) and any internal standards from the collective concentration of any range in which they elute. If the recommended surrogate 2,5-dibromotoluene is used, no correction is necessary, as this compound elutes after all ranges of interest.

12.3.4 Subtract the collective concentration of $C_9 - C_{12}$ Aromatic Hydrocarbons from the collective concentration of $C_9 - C_{12}$ Aliphatic Hydrocarbons. If this value is less than the reporting limit, report "not detected".

12.3.5 Subtract the individual concentrations of the VPH Target Analytes from the appropriate Aliphatic range (i.e. $C_5 - C_8$ or $C_9 - C_{12}$ Aliphatic Hydrocarbons) in which they elute. It the individual concentrations of Target Analytes have been quantified using another method (e.g. by using an MS detector), note this on the data report form. If the individual concentrations of Target Analytes have not been quantified, report the values as unjustified $C_5 - C_8$ Aliphatic Hydrocarbons and unjustified $C_9 - C_{12}$ Aliphatic Hydrocarbons, and indicate "not determined" for $C_5 - C_8$ Aliphatic Hydrocarbons and $C_9 - C_{12}$ Aliphatic Hydrocarbons.

13.0 METHOD PERFORMANCE

Method Detection Limit (MDL) Study

The MDL study is a statistically derived assessment of method performance with respect to the variance in the production of extracts and their analysis. Method detection limits are calculated using the folllowing formula:

$$\mathrm{MDL} = S\, t_{(n-1,\ 1-\mathrm{alpha} = 0.99)}$$

Where:
S = the standard deviation of the replicate analyses
n = number of replicates
$t_{(n-1,\ 1-\mathrm{alpha} = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult “Less is Better: Laboratory Chemical Management for Waste Reduction”, available from the American Chemical Society’s Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.0 DATA ASSESSMENT AND CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Technical acceptance criteria for sample analysis.

15.1.1 The samples must be analyzed on a GC system meeting the initial calibration, continuing calibration and blank technical acceptance criteria.

15.1.2 The sample must be analyzed within the required holding time.

15.1.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

15.1.4 The percent recovery of each of the system monitoring compounds in the sample must be within the acceptance windows.

15.1.5 The retention time shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the sample and the most recent continuing calibration standard analysis.

15.1.6 After analyzing a sample that exceeds the initial calibration range the analyst must either analyze an instrument blank (using the same purge inlet if using an auto sampler) which must meet technical acceptance criteria for blank analysis or monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the calibration range. The maximum contamination criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds that exceeded the limits in the contaminated sample. If auto sampler is used, the next sample analyzed using the same purge inlet must also meet the maximum contamination criteria. If the maximum criteria is exceeded then all samples affected by the carryover must be re-analyzed.

15.2 Corrective Action for Sample Analysis

15.2.1 Samples must meet technical acceptance criteria before reporting data.

15.2.2 Corrective action for failure to meet instrument performance checks, initial, continuing calibration and method blanks must be completed prior to sample analysis.

15.2.3 Corrective action for system monitoring compounds and internal standard compounds that fail to meet acceptance criteria must be completed prior to sample analysis.

15.3 If any of the system monitoring compounds and internal standard compounds fail to meet acceptance criteria:

15.3.1 Check all calculations, instrument logs, the system monitoring compound and internal standard compound spiking solutions and the instrument operation. If the calculations were incorrect, correct calculations and verify that the system monitoring compound recoveries and internal standard compound responses meet acceptance criteria. If the instrument log for the amount of internal standard compound spiking solution that was added. If an incorrect amount was spiked reanalyze with the correct amount.

15.3.2 Check the preparation of the internal standards and system monitoring compounds for concentration and expiration.

15.3.3 Verify that the instrument is operating correctly.

15.4 Determine if the problem was a matrix effect.

15.4.1 Check the surrogate recoveries for the MS and MSD.

15.4.2 If the system monitoring compound recoveries and the internal standard compound recoveries meet the acceptance criteria in the reanalyzed samples, the samples are considered in control and the data may be reported.

15.4.3 If the system monitoring compound recoveries and the internal standard compound responses do not meet the acceptance criteria in the reanalyzed samples, then submit data from both analyses.

16.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. Data qualifiers can be found in Section 19.0. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up.

17.0 WASTE MANAGEMENT

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water and land by minimizing and controlling all release from hoods, and bench operations, complying with the letter and spirit of any waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

18.0 REFERENCES

Method for the Determination of Volatile Petroleum Hydrocarbons (VPH), Massachusetts Department of Environmental Protection, January 1998

19.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION FORMS

Table 10: Compound List and Reporting Limits for Target Aromatic Hydrocarbons

Analyte	**Water (ug/L)**	**Soil (ug/Kg)**
methyl-tert-butylether	15	~~780~~ 750
benzene	5.0	~~260~~ 250
toluene	15	~~780~~ 750
ethylbenzene	5.0	~~260~~ 250
p+m xylene	20	1000
o-xylene	10	~~520~~ 500
naphthalene	10	~~520~~ 500

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Table 11: Compound List and Reporting Limits for Petroleum Hydrocarbons Ranges

Analyte	Water (μg/L)	Soil (μg/Kg)
$C_5 - C_8$	~~10~~ 40	~~520~~ 2040
$C_9 - C_{12}$	10	~~520~~ ~~500~~ 510
$C_9 - C_{10}$	~~11~~ 10	~~520~~ 500

Standard Data Qualifiers

U = Compounds not detected at or above reporting limit.
E = Compound concentration exceeds the calibration range.
D = Compound concentration is reported from a secondary dilution of the sample.

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METHOD VPH_MA
STANDARD OPERATING PROCEDURE FOR VOLATILE PETROLEUM HYDROCARBONS-MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION BY GAS CHROMATOGRAPHY

Applicable Matrix or Matrices: Waters, Soils, and Sediments
Standard Compound List and Reporting Limits: See Appendix A

Approvals and Signatures

Laboratory Director: Christopher A. Ouellette Date: 8/8/00

QA Manager: Kim B. Watson
Kim B. Watson Date: 8/8/00

Organic Technical Director: Bryce E. Stearns Date: 8/8/00

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1.0 SCOPE AND APPLICATION

This method is used to determine the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil samples. Volatile aliphatic hydrocarbons are collectively quantitated within two ranges: C5 through C8 and C9 through C12. Volatile aromatic hydrocarbons are collectively quantitated within the C9 to C10 range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36° C and 220°C. Individual concentrations of

Form 1

VOLATILE PETROLEUM HYDROCARBON (VPH) ANALYSIS

Lab Name:	STL		**Contract:**	98004
Lab Code:	INCHVT		**Case:**	E0778
Matrix:	WATER	(soil/water)	**SDG:**	71479
Sample wt/vol:	5.00	ML	**Client ID:**	VBLKL4
% Moisture:	_	(%)	**Lab Sample ID:**	VBLKL4
Level:	LOW	(low/med)	**Date Received:**	____
Extract Volume:	_	(ml)	Date Analyzed:	12/7/98
GC Column:	RTX-502.2		Dilution Factor:	1
Column ID:	0.53		**Soil Aliquot Volume:**	__
Conc Units:	UG/L			

CAS NO.	Analyte	Amount	Q	
1634-04-4	Methyl tert-Butyl Ether	15	U	
71-43-2	Benzene	5.0	U	
108-88-3	Toluene	15	U	
100-41-4	Ethylbenzene	5.0	U	
1330-20-7	p/m-Xylene	20	U	
95-47-6	o-Xylene	10	U	
91-20-3	Naphthalene	10	U	

VPH Totals	Amount	Q
C5-C8 Aliphatics (FID) 1	40	U
C9-C12 Aliphatics (FID) 1	10	U
C9-C10 Aromatics (PID) 1	11	U
C5-C8 Aliphatics (FID) 1,2	40	U
C9-C12 Aliphatics (FID) 1,3	10	U

1 - Hydrocarbon Range data exclude concentartions of any surrogates

2 - C5-C8 Aliphatic Hydrocarbons exclude the concentration of Target Analytes eluting in that range

3 - C9-C12 Aliphatic Hydrocarbons exclude conc ot Target Analytes eluting in that range AND concentration of C9-C11 Aromatic Hydrocarbons.

SAMPLE INFORMATION:

Containers: Satisfactory_____ Broken_____ Leaking_____
Aqueous: N/A_____ pH ≤ 2_____ pH >2 _____
Soil or Sediment: N/A_____ Samples NOT preserved in Methanol or air tight containers_____
Sample rec's in Methanol_____ covering soil_____ not covering soil_____
Sample Received in air- tight container_____ m/L Methanol/g soil: 1:1_____ Other _____
Temperature: Received on Ice_____ Received at 4C_____ Other_____

APPENDIX A-103

HYDROCARBON CHARACTERIZATION/FUEL FINGERPRINT ANALYSIS METHOD - MODIFIED 8015

HYDROCARBON CHARACTERIZATION/FUEL FINGERPRINT ANALYSIS METHOD - MODIFIED 8015

1.0 Purpose

To provide the procedures used to determine the concentration of fuel hydrocarbons (C6-C36) in solid and aqueous matrices.

2.0 Scope

Applies to all solid and aqueous matrices analyzed by this procedure in the GC/Organics laboratory. This procedure is used to detect the following substances:

2.1 Gasoline

2.2 Diesel

2.3 Jet fuel

2.4 Paint thinner

2.5 Kerosene

2.6 Stoddard solvent

2.7 Mineral spirits

3.0 Summary of method

This method provides an extraction procedure and the chromatographic conditions for the detection of a fuel hydrocarbon in the carbon range of C6-C36. A weighed amount of the solid matrix is extracted using methylene chloride as the extraction solvent. A measured volume of aqueous matrix is extracted with methylene chloride. Quantitative analysis is done using direct injection of 1.0 µl of organic solvent extract into a gas chromatograph (GC). A temperature program is used in the GC to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

4.0 Responsibilities

4.1 It is the responsibility of the departmental supervisor to ensure all departmental chemists and technicians are trained and adhere to the guidelines and procedures outlined in this SOP.

4.2 It is the responsibility of all departmental chemists and technicians to adhere to the guidelines and procedures outlined in this SOP.

4.3 It is the responsibility of the departmental supervisor, chemists, and technicians to ensure that this SOP actually reflects what is being performed in the laboratory.

5.0 References

5.1 This SOP is based in part on Method 8015A, SW846, Third Edition, Update I, July 1992.

5.2 This SOP is based in part on Method 8015B, SW846, Third Edition, Update III, December 1996.

5.3 For operation of the GC and software, refer to the Hewlett Packard Manuals, HP 5890, Series II GC Operation Manual and Reference Manual and Hewlett Packard Reference Manuals Volume I and Volume II (HP 3365).

6.0 Preservation and Holding Times

See STL-PN SOP 1040 (Sample Preservation and Holding Times) for applicable preservation and holding time requirements.

7.0 Apparatus

7.1 Gas chromatograph HP 5890 flame ionization detector (FID).

7.2 Integrator

7.3 GC capillary RTX-5 30 m X 0.53 or equivalent

7.4 Mettler balance (top loader)

7.5 Aluminum weighing boats

7.6 2000 ml separatory funnels

7.7 500 ml K-D flasks with 10 ml concentration tubes

7.8 Spatula

7.9 Snyder columns (3 balls)

7.10 Water bath

7.11 Sonic disrupter

7.12 250 ml beaker

7.13 Syringes (10 µl, 50 µl, 100 µl and 500 µl)

7.14 Autosampler vials - 1 ml

8.0 Reagents

4.1 Methylene chloride - Pesticide quality

4.2 Sodium sulfate (Na_2SO_4) - granular, kiln dried

9.0 Standards

9.1 Diesel, gasoline, mineral spirits, JP-4, JP-5 (if expected at site), DRO (diesel range organics) and any other required standards, prepared at appropriate concentrations. DRO standard used for a five point curve at concentrations of 5, 20, 50, 100, and 200 ppm. A 100 ppm continuing calibration is analyzed daily with samples.

9.2 Diesel spike - obtained from local service station. Prepare diesel spike by making 100 mls of 10000 ppm diesel.

9.3 Upon request, NIST or EPA-traceable standards will be used to verify calibrations.

9.4 Acceptance limits for standards that are to be analyzed every 10 samples will be based on the same %D criteria specified in the referenced method.

9.5 Surrgogates used are Ortho-terphenyl and 4-Bromofluorobenzene. Prepare at appropriate concentration in methylene chloride (see STL-PN 8015 standard log book).

10.0 Extraction Procedures

10.1 Aqueous Sample Extraction

Measure 1 L of aqueous sample into a 2 L separatory funnel. Spike with 1 ml of 250 ppm surrogate. Extract sample three times using 60 ml methylene chloride and shake for five minutes for each extraction. Combine extractions in 500 ml K-D flask in water bath at 70°C and concentrate sample to 5 ml. Cool and transfer sample to 4 ml Wheaton vial. See STL-PN SOP 304 [Separatory Funnel Liquid-Liquid Extraction (3510C)] for additional information.

10.2 Solid Sample Extraction

Weigh 30 grams of soil sample into 25 beaker, add 0.5 Na_2SO_4, mix with sample. Spike with 1 ml of 250 ppm surrogate. Extract 3 times using 100 mls methylene chloride and sonicate for 1 ½ minutes for each extraction. Combine extracts in 500 ml K-D flasks in water bath at 70°C and concentrate sample to 5 ml. Cool and transfer sample to 4 ml Wheaton vial. See STL-PN SOP 307 [Preparation of Soil/Sediment by Pulsed Sonication for the Analysis of Low Level Concentrations of Organic Compounds (Low Level Method)].

11.0 GC Column and Operating Conditions

11.1 Column RTX-5 capillary

11.2 Detector: flame ionization detector

11.3 Injection method: Splitless mode with vent time at 0.5.

11.4 Program temperature:

Initial temperature = 40°C, hold = 2 minutes.
Rate = 12°C/min to 320°C, hold 15 minutes.
Total Run time 40.33 minutes.

11.5 Gas flows:

Hydrogen	= 30 ml/minute
Air	= 300 ml/minute
Slit (He)	= 100 ml/minute
Septum Sweep	= 5 ml/minute

11.6 Column pressure = 15 psi

11.7 All parameters are identical for the dual system.

12.0 Sample Loading

Samples are placed in 1 ml autosampler vials and put on the autosampler in the following sequence: First, a methylene chloride blank to establish a solvent baseline; next, a 100 ppm DRO calibration check standard followed by a 250 ppm OTP surrogate standard. Lastly, the extracted soil and/or water samples with the required QC are loaded. For TCO's a standard is analyzed which has a fingerprint that most closely matches the samples. A 300 ppm diesel standard is also run daily along with the samples.

13.0 Calibration

13.1 Calibrate using the external standard calibration technique. Prepare DRO calibration standards at five concentration levels: 5, 20, 50, 100 and 200 ppm. The concentrations correspond to the working range of the detector. The 200 ppm concentration is at the high end of the linear range.

13.2 The 5 concentration levels of DRO standard are prepared in methylene chloride.

13.3 Using a 1.0 µl injection of each of the calibration standards, calculate the ratio of the response to the mass injected of the standard on the column which is defined as calibration factor (CF). The calibration curve is linear if the relative standard deviation (RSD) of the calibration factor is less than or equal to 15% (RSD < 15%), or if the correlation coefficient is 0.995 or better.

13.4 The working calibration curve is verified every 24 hours by the measurement of the 100 ppm midpoint of the DRO standard. If the response varies more than ± 15% or the correlation coefficient is <0.995 the analysis is repeated using a fresh calibration standard. If this response does not meet criteria, a new calibration curve is analyzed.

14.0 Analysis

14.1 Inject 1.0 µl of the methylene chloride extract of the sample into the GC.

14.2 If the peak areas or peak height exceed the linear range of the system, dilute the extract and analyze again. The acceptance criteria for linearity is a correlation coefficient of 0.995 or greater.

14.3 Quantitation is done by ratio of total peak areas. Integration is started after the solvent peak returns to base line. If significant peaks appear as shoulders on the solvent peaks, these peaks can be included in the total area at the discretion of the analyst.

14.4 All chromatograms are manually inspected by the analyst to insure that extraneous background peaks (obvious non-petroleum hydrocarbon peaks) are not included in the total area calculation of the sample. These peaks will be notated as unidentifiable.

14.5 All QC is quantitated using a DRO standard against a Diesel spike, providing a secondary standard source.

14.6 TCO's: Chromatograms are identified by fingerprint. A standard that most closely matches the sample fingerprint is used for quantitation purposes. If a sample is determined to be unidentifiable, a standard which most closely matches the carbon range is used to quantitate the sample and an unidentifiable carbon range notation is attached to the sample. All samples are integrated using total area. If the OTP surrogate falls within the area range, it is subtracted from the total area.

14.7 DRO's: Chromatograms are quantitated using a DRO standard. The carbon range is determined by the state method requirement:

Tennessee DRO	C10-C28
Mississippi DRO	C10-C25
Arizona DRO	C10-C22

NOTE

An agency in each state should be contacted for their DRO definition. The corresponding retention times for the beginning and end of each range is determined from the CC. The total area between the carbon range needed is used to quantitate against the corresponding total area of the samples. Since the surrogate OTP falls in between the DRO carbon range, it is subtracted from the total area.

RIDRO(Rhode Island Diesel Range Organics)

Chromatograms are quantitated using fuel oil #2 or diesel using valley-to-valley integration. Extraction for soils uses freon as the solvent and includes a silica gel clean-up step in between extraction and boil-down to 5 mls. This is per RIDRO method as determined by New England Testing Laboratory, Inc.

14.8 Procedures in this SOP may differ depending on contractual requirements. STL-PN will strive to meet any state-specific, client-specific, or consent decree requirements requested. Specific instructions will be issued when these situations occur.

15.0 Quality Control

15.1 Quality Control deals with the overall quality of the data output. The instrument is monitored each day of use. If a monitored parameter is not acceptable, it is considered out of control. An out of control event may result in reanalysis of client and/or QC samples. Written documentation is required when an unacceptable result is accepted due to matrix affect or other uncontrollable circumstances per STL-PN SOP 1060. See STL-PN SOPs 1060 [Protocol for Out of Control Events (OOCE)] and 1061 (Corrective Action Documentation Requirements) for procedures to follow when QC fails and action to take for situations requiring corrective action forms.

15.2 Samples are prepared and analyzed in QC batches. A QC batch is a group of similar matrices (aqueous, solid, oil) processed together. Samples that do not require digestion, distillation or extraction are batched by the analytical departments. Samples that require digestion, distillation or extraction are batched by the digestion, distillation or extraction departments. Unless specified by the client or regulatory agency, STL-PN allows batches to contain 20 client samples or be 3 days long, whichever comes first. STL-PN will limit batches to one day with a maximum of 20 samples as required by AFCEE, NFESC, state of Arizona and any other client or regulatory agency which requires that batches be limited to the number of samples processed at one time. At a minimum, each QC batch shall also contain a matrix-specific method or extraction blank for each day samples are analyzed or prepared, a matrix-specific Laboratory Control Sample (LCS), and a matrix spike and matrix spike duplicate.

15.3 The blank is analyzed to insure the instrument is contamination free. The instrument must be considered contaminant-free prior to analyzing any samples. Each time a set of samples is extracted or there is a change in reagents, a method blank is analyzed to check for laboratory contamination. Method blanks are carried through all stages of the sample preparation (extraction) and analysis procedures. See STL-PN SOPs 1060 and 1061 for action to be taken when the blank fails acceptance criteria."

15.4 An LCS is reagent water or Ottawa sand to which target compounds at known concentrations are spiked to determine if the preparation and/or analytical process is in control. See STL-PN SOPs 1060 and 1061 for action to be taken when the LCS fails acceptance criteria.

15.5 Matrix spike compounds at known concentrations are spiked into a sample and duplicated to determine the matrix effects of the sample on recovery of the compounds. See STL-PN SOPs 1060 and 1061 for action to be taken when the MS/MSD fails acceptance criteria. The spiking levels of fuel hydrocarbons are 330 mg/kg for soils and 10000 µg/l for waters.

15.6 The spiking solution for the LCS, MS and MSD is prepared by the GC/Organic chemist and delivered to the extractions department. The spiking solution is then added to reagent water for the LCS by the extractions technician. Triplicate one liter samples are then selected and the spiking solution is spiked into two duplicate samples by the extractions technician prior to extraction of the MS and MSD. The third sample is extracted and analyzed without spiking. Target compounds and concentrations may vary per individual client request.

15.7 Surrogate spike recoveries are calculated for each blank, LCS, MS, MSD, and sample. Surrogate recoveries are evaluated against in-house calculated control limits. The surrogate spiking solution is prepared by the GC/Organic analyst and delivered to the extractions department. The extractions department technician then spikes all samples and QC samples with 1 ml of the surrogate spiking solution prior to extraction. The true value for the surrogate is 50 ppm.

15.8 Method Detection Limit (MDL) studies are calculated annually. See STL-PN SOP 1004 (Analysis, Documentation, and Review of MDL, IDL and P&A Studies). MDL studies are reviewed and maintained on file in STL-PN's QA department.

15.9 Control limits are listed in section 5.0 of STL-PN's CompQAP. Refer to STL-PN SOP 1003 (Calculation of Annual Control Limits). Because control limits may have been updated since the last CompQAP update, the most current departmental control limits are on file in STL-PN's QA department.

15.10 Refer to STL-Pensacola's CompQAP, section 11 for QC calculations.

16.0 Calculations and Reporting

16.1 The concentration of hydrocarbons in an extracted sample is calculated by using a total area sum.

$$\frac{\text{(area sample) X conc. std.}}{\text{(area std.)}} \quad \text{X} \quad \frac{\text{final vol.}}{\text{initial vol.}} \quad \text{X dilution factor}$$

(use initial weight instead of initial vol. for soils)

Area of OTP surrogate is then subtracted when applicable.

16.2 Soils are reported in mg/kg by dry weight with a reporting limit of 2.5 mg/kg. RIDRO soils have a reporting limit of 5.0 mg/kg. Waters are reported in ug/l with a reporting limit of 100 μg/l. All samples below the reporting limits are reported as ND (Not Detected).

16.3 The data report to the client includes TPH result(s), identity of the standard used for quantitation, the surrogate recovery and the acceptable recovery limits, a brief narrative consisting of the hydrocarbon range found (if necessary), an identification of the fuel found (if possible), and the presence of any obvious non-petroleum interferences whose areas are included in the result(s).

16.4 Normal reporting limits are listed in STL-PN CompQAP Section 5. Reporting limits may be elevated due to a necessary dilution or client request. See STL-PN SOP 2001 (Dilution of Samples).

16.5 Refer to STL-PN CompQAP Section 12 for data reporting.

16.6 Refer to STL-PN CompQAP Section 12 and STL-PN SOP 2008 (Records Management in the Laboratory) for data storage.

16.7 Refer to STL-PN CompQAP section 7 for sample tracking.

17.0 Maintenance

17.1 A maintenance log book is kept for the GC instrument running the Modified 8015 method.

17.2 Refer to the instrument operating manual for maintenance requirements and suggestions.

17.3 Refer to STL-PN CompQAP Section 10 for the maintenance schedule. Refer to STL-PN SOP 2005 (Instrument Maintenance Documentation) for maintenance criteria and maintenance documentation.

18.0 Sample and Waste Disposal

Sample and waste disposal is described in STL-PN SOP 1800 (Waste Handling and Disposal). Sample and waste disposal is also discussed in STL-PN CompQAP, sections 7 and 8.

19.0 Maintenance of Electronic Data Files

Data files are stored on the computer for a period of 60 to 90 days or until the file storage interferes with daily operation.

INSTRUMENT SET UP AND OPERATING CONDITIONS FOR EPA MODIFIED SW8015

1. Column RTX-5 capillary

2. Detector: flame ionization detector

3. Injection method: Splitless mode with vent time at 0.5.

4. Program temperature:

   Initial temperature = 40 °C, hold = 2 minutes.
   Rate = 12 °C /min to 320 °C, hold 15 minutes.
   Total Run time 40.33 minutes.

5. Gas flows:

   Hydrogen = 30 ml/minute
   Air = 300 ml/minute
   Slit (He) = 100 ml/minute
   Septum Sweep = 5 ml/minute

6. Column pressure = 15 psi

7. All parameters are identical for the dual system.