O'Reilly, Talbot & Okun
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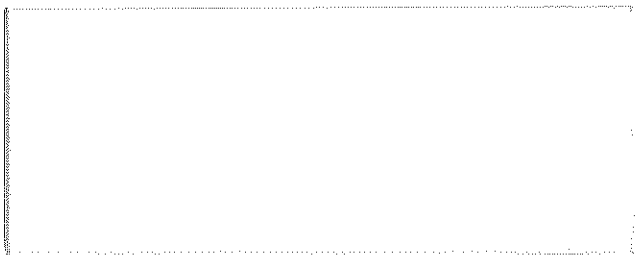

October 29, 2002
J076-22-02

Prepared For:

Springfield Planning Department
36 Court Street
Springfield, Massachusetts

Attn: Ms. Katie Galuzzo

Quality Assurance Project Plan Addendum

Indian Orchard Brownfields Site
225 Goodwin Street
Springfield, Massachusetts

Prepared By:

O'Reilly, Talbot & Okun Associates, Inc.
293 Bridge Street, Suite 500
Springfield, Massachusetts 01103

EnvironmentalSafetyHealthGeotechnical

O'Reilly, Talbot & Okun
[ASSOCIATES]
ENGINEERING

293 Bridge Street
Suite 500
Springfield, MA 01103
Tel 413 788 6222
Fax 413 788 8830
Email office@oto-env.com

J076-22-02
October 29, 2002

Springfield Planning Department
36 Court Street
Springfield, Massachusetts 01103
Attn.: Ms. Katie Galuzzo

Re: Quality Assurance Project Plan Addendum
Indian Orchard Brownfields Site
225 Goodwin Street
Springfield, MA

Dear Ms. Galuzzo:

Attached please find the Addendum to the Quality Assurance Project Plan (QAPP) for the above-referenced Brownfields site. This addendum covers supplemental field work that is planned in support of the Massachusetts Contingency Plan (MCP) Phase II/III investigations and report. This plan was prepared by O'Reilly, Talbot & Okun Associates, Inc. (OTO) for submittal to the Region I U.S. Environmental Protection Agency (EPA). This addendum will be revised, if necessary, following receipt of comments from EPA and the City of Springfield. Field work will be initiated once the QAPP Addendum has been finalized.

If you have any questions please do not hesitate to contact us.

Very truly yours,
O'Reilly, Talbot & Okun Associates, Inc.

Michael J. Talbot, LSP, PE
Principal

cc: Joseph Ferrari/EPA

F:J0001/76 City of Springfield/Crane QAPP Addendum

TITLE AND APPROVALS PAGE

Title: Quality Assurance Project Plan; Indian Orchard Brownfield Site, Springfield MA

Prepared By: O'Reilly, Talbot & Okun Associates, Inc.
293 Bridge Street, Suite 500
Springfield, Massachusetts 01103
(413) 788-6222

Project Manager: _____
Signature

10/31/02

Michael J. Talbot
Printed Name/Date

Project QA Officer: Valerie Watanabe 10/31/02
Signature

Valerie D. Watanabe
Printed Name/Date

U.S. EPA Project Manager Approval: _____
Signature

Joseph Ferrari
Printed Name/Date

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FIGURES

APPENDICES

1.00 INTRODUCTION

This document provides an addendum to the Quality Assurance Project Plan (QAPP) for environmental investigations at the Indian Orchard Brownfields site in Springfield, Massachusetts. A site locus map is provided as Figure 1. Revisions 0 and 1 of this QAPP were dated May 22 and June 13, 2000, respectively. This addendum (also known as Revision 2 of the QAPP) covers supplemental investigations planned for the site in support of the Massachusetts Contingency Plan (MCP) Phase II Comprehensive Site Investigation and Phase III Remedial Action Plan.

This QAPP has been reviewed and approved by the signatories identified on the attached Title and Approval Page. If conditions arise requiring additional changes to the plan, those changes will undergo the same review and approval as the original QAPP.

Personnel working on this project must understand that they bear individual responsibility for performing the work in accordance with the QAPP. If questions arise as to the methods used or acceptability of alternative methods, staff should discuss plans and alternatives with their supervisor and/or the QA Officer. The Project Manager and other key contacts are identified on the organizational chart provided as Table 1, which provides contact names, organizational affiliations and telephone numbers, and the chain of command for this project. Some of the contacts on Table 1 have changed since the original QAPP was issued; an updated Table 1 is attached.

2.00 BACKGROUND INFORMATION/PROBLEM DEFINITION

The subject site is an 11.9 acre parcel that was part of the former Chapman Valve (Crane Company) manufacturing complex beginning in the 1920s. Chapman Valve/Crane Company operated a steel foundry in the site building from 1942 until 1983. Between 1985 and 1989 American Dream Homes manufactured modular homes on the property. The City of Springfield now owns this property and wishes to redevelop it for commercial/industrial use.

The original QAPP covered environmental investigations conducted at the site in 2000 and 2001. Those investigations indicated site soil and groundwater have been impacted by chlorinated volatile organic compounds (VOCs) and petroleum. The extent of impacts from these constituents was not fully delineated during the initial studies. This QAPP covers additional investigations proposed to complete characterization of the nature and extent of impacts, and to support an evaluation of potential remedial alternatives.

3.00 PROJECT DESCRIPTION

The current phase of work will involve investigation on two portions of this Brownfields site: the former Crane Company Steel foundry at 225 Goodwin Street, and the property at 121 Pinevale Street. The following tasks have been proposed:

1. Supplemental soil borings and monitoring well installations in areas of concern;
2. Chemical analysis of soil and groundwater samples;
3. Development of groundwater contour plans;
4. Preparation of an MCP Phase II/Phase III report, to include a summary of investigations, risk characterization, and remedial action plans for the property.

Data collection tasks are described in further detail below. Proposed investigation locations are shown on Figures 2 and 3. Table 2 provides an estimated project schedule. The actual dates of the tasks shown may change; field work will begin upon approval of the QAPP.

3.10 SAMPLING DESIGN

Sample collection and handling methods to be used during this phase of investigation are the same as those used in the previous phase. Activities will be consistent with the SOPs provided in the March 2000 QAPP.

3.11 Soil Borings/Soil Sampling

A licensed drilling contractor will be retained to perform approximately 10 borings using standard hollow stem auger drilling techniques. Two of the borings will be completed as groundwater monitoring wells. Approximate boring/monitoring well locations are shown on Figure 2. Locations were selected as follows:

- At the Goodwin Street site, one 20 to 25 foot boring will be located northwest of existing well CEA-2. That boring will be completed as a monitoring well to provide information on the downgradient limits of groundwater impacts.
- Four shallow borings will be performed through the 225 Goodwin Street floorslab in the vicinity of former underground storage tanks to evaluate the extent of petroleum impact beneath the building.
- At the Pinevale Street Site, five shallow borings are proposed to define the limits of surficial contamination identified near the northwest corner of the site building. One of these borings will be completed as a monitoring well to assess potential groundwater impacts in that area.

Soil samples will be collected at intervals of 5-feet or less using a split spoon sampling device. Soil samples will be screened in the field for the presence of VOCs using a photo-ionization detector (PID). Selected samples will be retained for quantitative laboratory analysis by state certified laboratory. Samples will be selected based upon location, field observations and field screening results. The proposed testing program for soil is outlined below.

Proposed Soil Analytical Program

Parameters	Methodology	Number of Samples
Goodwin Street: Petroleum Hydrocarbons	Massachusetts EPH	4 soils (1 per boring)
Pinevale Street: Petroleum Hydrocarbons Volatile Organic Compounds	Massachusetts EPH Massachusetts VPH EPA Method 8260	5 soils (1 per boring)
QA/QC Samples: Petroleum Hydrocarbons Volatile Organic Compounds	Massachusetts EPH Massachusetts VPH EPA Method 8260	1 field duplicate 1 equipment blank 1 PES 1 trip blank per cooler 1 temp. blank per cooler

Drill cuttings will be screened in the field using the PID. If drill cuttings exhibit an oil or solvent odor, exhibit a PID response greater than 50 meter units or if the soils are observed to be stained or contain potential metal bearing wastes they will be placed in 55-gallon drums and analyzed further for subsequent disposal. If the soil cuttings are not visibly stained or odorous and do not exhibit elevated PID readings they will be spread on the ground in the vicinity of the boring.

3.12 Groundwater Sampling

Following a one to two week stabilization period, groundwater samples will be collected from the two newly installed monitoring wells using methodology consistent with previously submitted SOPs. Existing wells OTO-1, CEA-2 and CEA-4 will also be sampled. The samples will be analyzed by AMRO, a State certified laboratory, for the parameters identified below.

Proposed Groundwater Analytical Program

Parameter	Methodology	Number of Samples
Petroleum Hydrocarbons	Massachusetts EPH Massachusetts VPH	5 groundwater 1 field duplicate 1 equipment blank 1 trip blank per cooler 1 temp. blank per cooler

In addition to the field samples, various quality assurance/quality control (QA/QC) samples will be submitted to the laboratory, as shown on the above two tables. The proposed number and type of field QC samples to be collected during this phase of work is consistent with the requirements of Table 11a in the original QAPP.

Chemical analyses for this project will be performed by AMRO Environmental Laboratories of Merrimack, New Hampshire. AMRO's standard operating procedures (SOPs) for these methods have been revised since the initial QAPP submittal. Table 4 has been updated to reference the current SOPs. Copies of the updated SOPs and most recent annual method detection limit studies are provided in Appendix A.

Data validation, data usability assessment, and other tasks not specifically discussed in this addendum will be conducted consistent with the existing QAPP, last amended June 2000.

TABLES

Table 1
(EPA Appendix B)
Project Organization and Responsibility

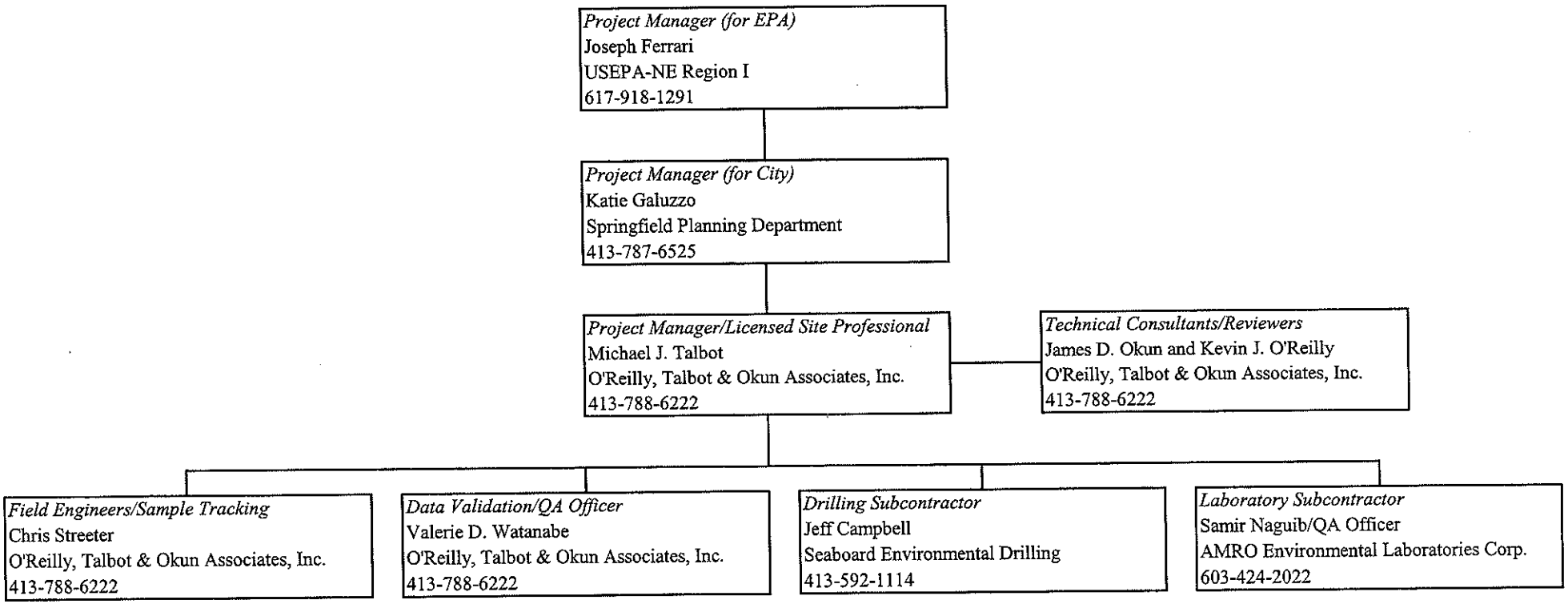


Table 2 (Addendum)
(EPA Appendix D, Cont.)
Project Timeline

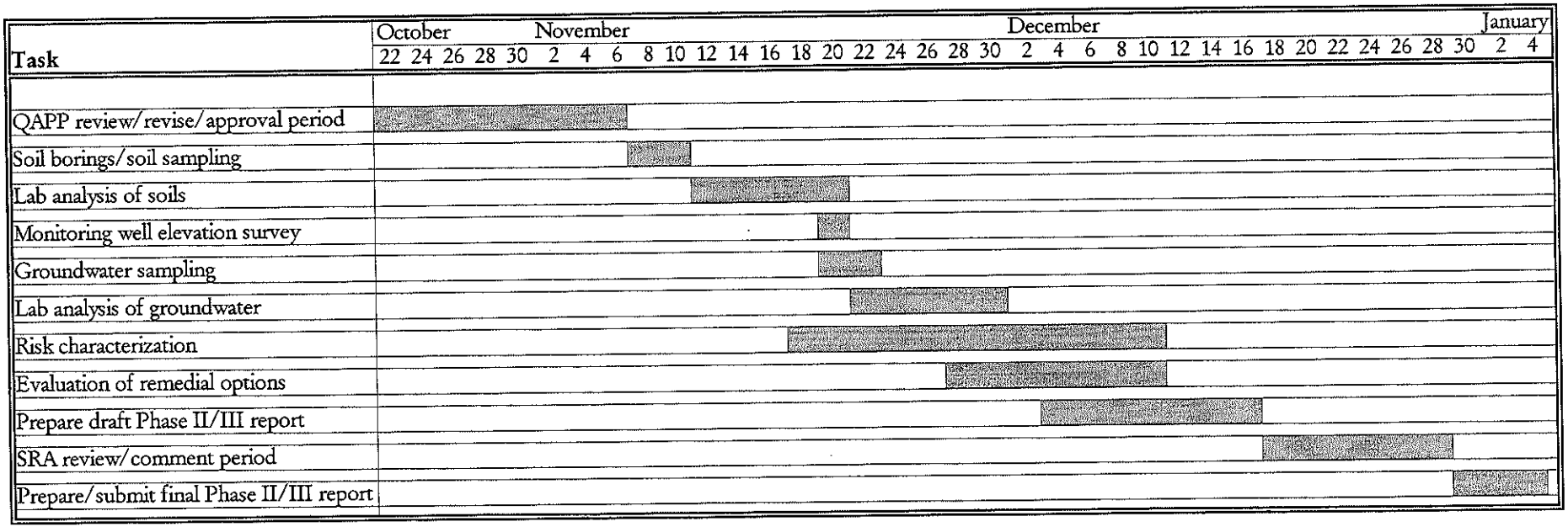
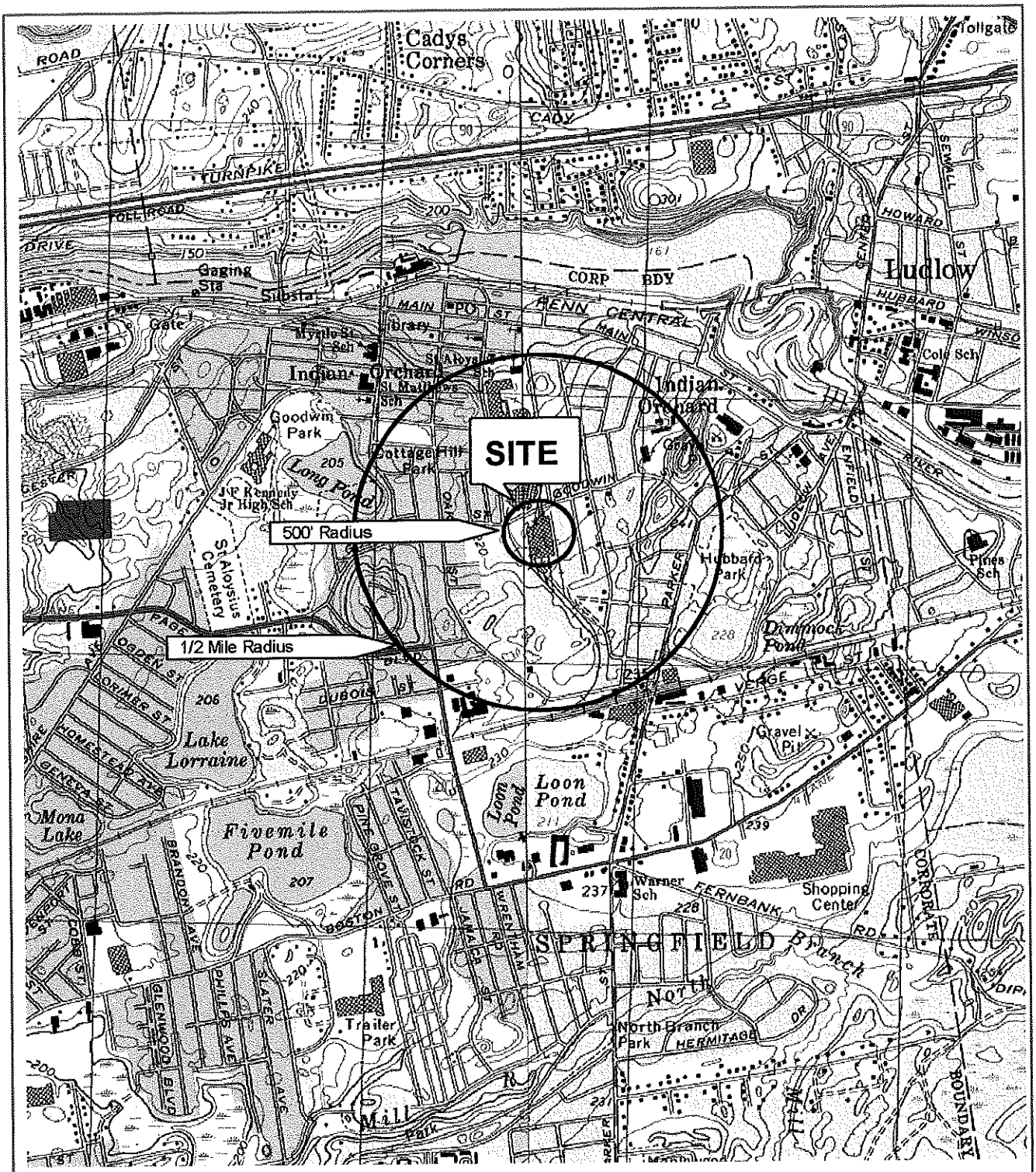


Table 4
(EPA Appendix F continued)
Method and SOP Reference Table

Analytical Method Reference: Include document title, method name/number, revision number, date	Project Analytical SOPs: Include Document title, date, revision number, and originator's name
1a. SW-846, Method 8260B, Rev. 2, 12/96	1b. Volatile Organics Analysis, SW-846 Method 8260B, 7/6/01, Rev. 6, AMRO Labs
2a. Method for the Determination of Volatile Petroleum Hydrocarbons (VPH), Public Comment Draft 1.0, August 1995, Mass. DEP	2b. Method for the Determination of Volatile Petroleum Hydrocarbons (VPH) by GC/MS, 4/3/01, Rev. 0,AMRO Labs
3a. Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), Public Comment Draft 1.0, August 1995, Mass. DEP	3b. Method for the Determination of Extractable Petroleum Hydrocarbons (EPH) Modified for GC/MS Analysis, 9/20/01, Rev. 1,AMRO Labs
4a. SW-846, Method 8082, Rev. 0, 12/96	4b. Polychlorinated Biphenyls (PCBs) using Method 8082, 2/27/99, Rev. 2, AMRO Labs
5a. SW-846, Method 3051, Rev. 0, 12/96	5b. Microwave Assisted Acid Digestion of...Soils according to EPA Method 3051, 8/21/98, Rev. 1, AMRO Labs
6a. SW-846, Method 3015, Rev. 0, 9/94	6b. Microwave Assisted Acid Digestion of Aqueous Samples according to EPA Method 3015, 7/17/98, Rev. 1, AMRO Labs
7a. SW-846, Method 6010B, Rev. 2, 12/96	7b. Analysis of Metals by Inductively Coupled Plasma Optical Emission Spectrometry according to EPA Methods 6010B, 3/1/99, Rev. 2, AMRO Labs
8a. SW-846, Method 7470A, Rev. 1, 9/94	8b. Determination of Mercury in Liquid Waste Samples according to EPA Method 7470A, 5/98, Rev.1 AMRO Labs
9a. SW-846, Method 7471A, Rev. 1, 9/94	9b. Determination of Mercury in Solid or Semisolid Waste Samples according to EPA Method 7471A, 3/1/99, Rev.2 AMRO Labs

Project Sampling SOPs: Include document title, date, revision number, and originator's name
1c. Hollow Stem Auger Overburden Drilling, SOP No. 2.1, Rev. 1, 1/24/00, OTO
2c. Model 580B Photoionization Detector, SOP No. 1.1, Rev. 1, 5/1/00, OTO
3c. pH Meter, SOP No. 1.2, Rev. 1, 5/1/00, OTO
4c. Specific Conductance Meter, SOP No. 1.3, Rev. 1, 1/6/00, OTO
5c. Groundwater Sample Collection by Bailer, SOP No. 3.3.1, Rev. 1, 5/1/00, OTO
6c. Sample Handling and Chain of Custody, SOP No. 3.0, 1/6/00, OTO



O'Reilly, Talbot & Okun Associates, Inc.

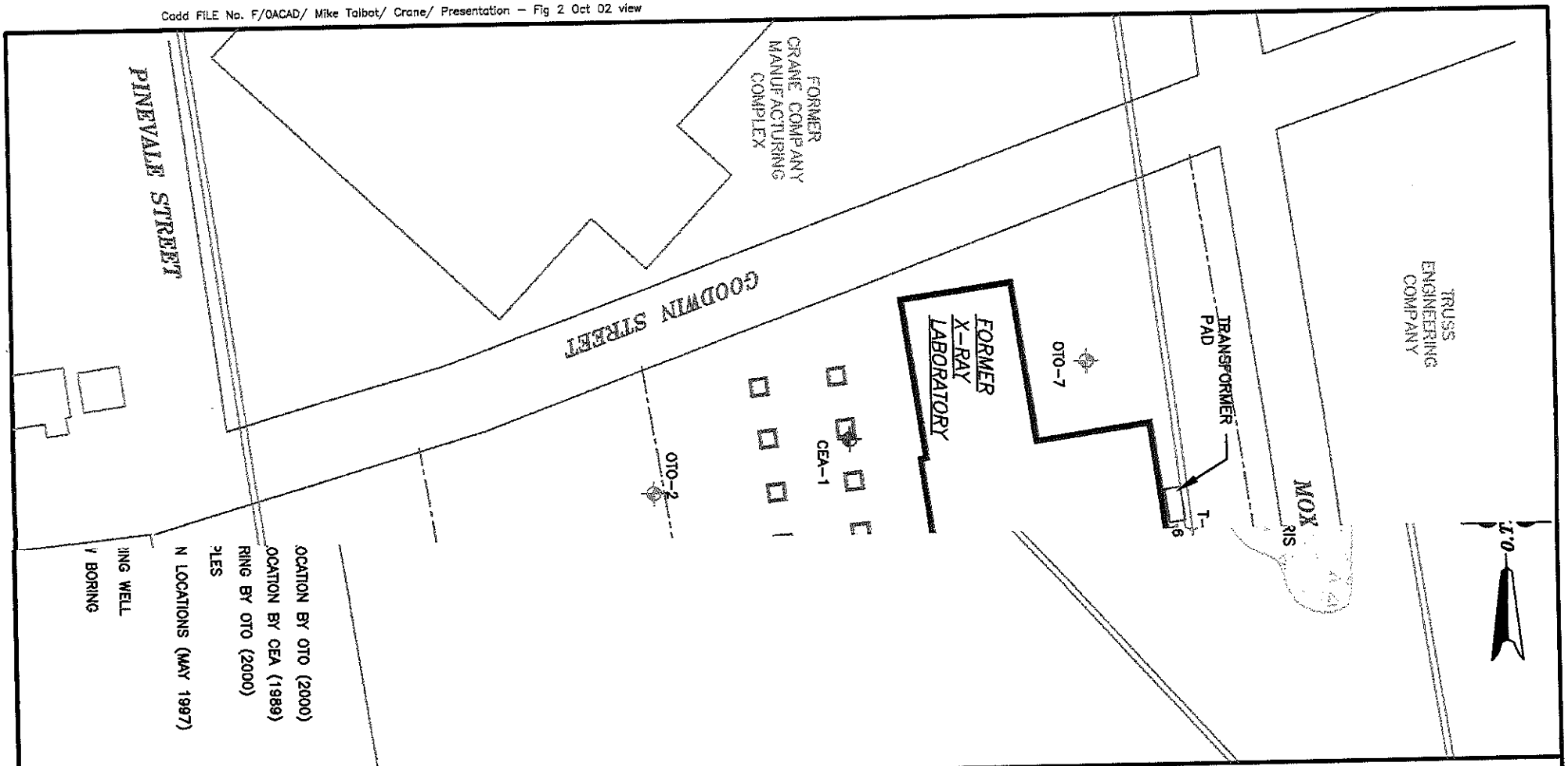
225 Goodwin Street
Springfield, Massachusetts

Site Locus

October 2002

Figure 1

Cadd FILE No. F/OACAD/ Mike Talbot/ Crane/ Presentation – Fig 2 Oct 02 view



FORMER CRANE BUILDING

SPRINGFIELD, MASSACHUSETTS

PROPOSED BORING LOCATIONS GOODWIN STREET SITE

SCALE IN FEET

1"= 80'

0' 40' 80' 160'

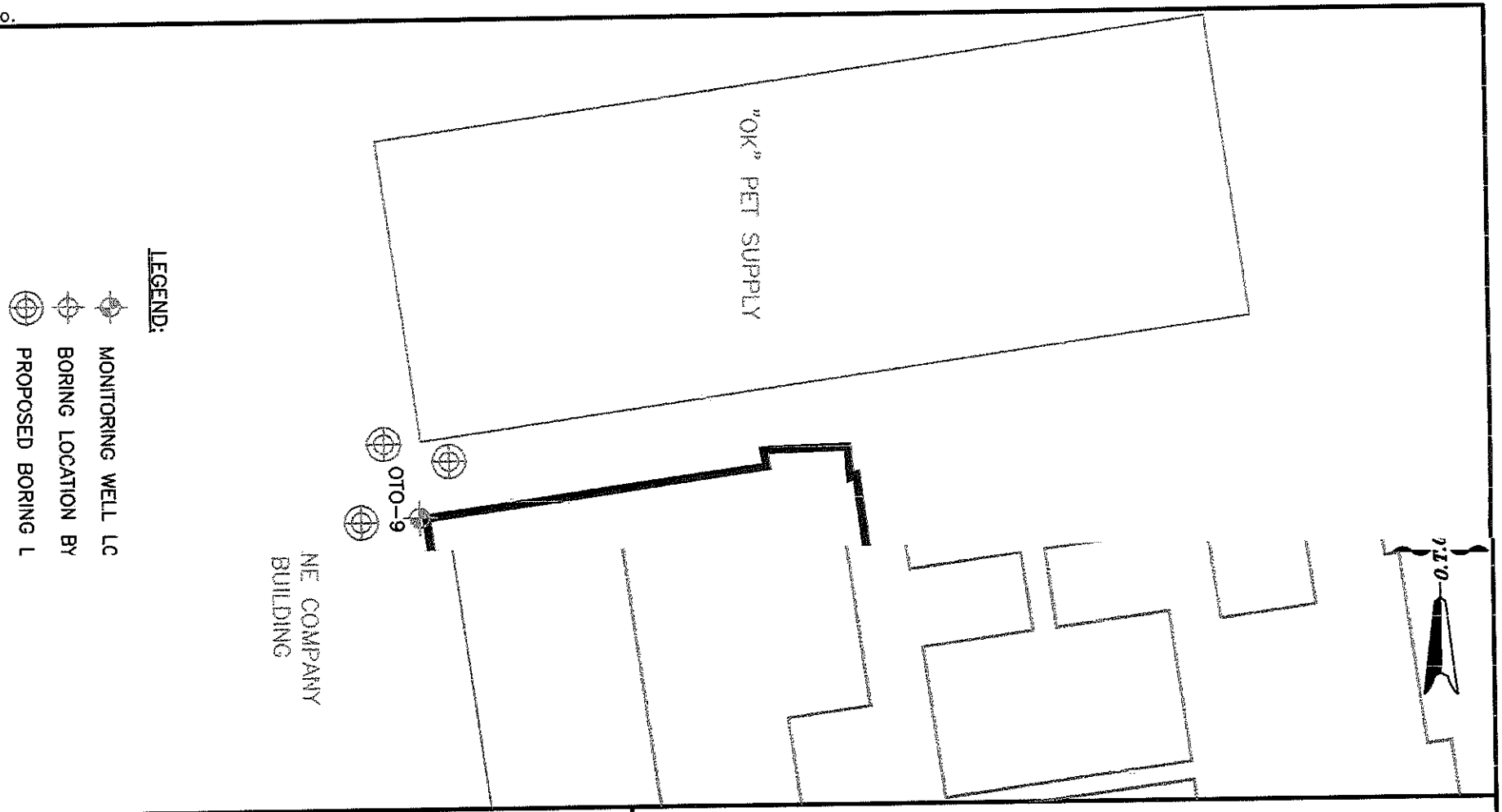
DESIGNED BY: JEG DRAWN BY: CDA
REVIEWED BY: DJM DATE: DEC. 5, 2000
REV: OCT. 28, 2002/ CDA

O'REILLY, TALBOT & OKUN ASSOCIATES, Inc.

PROJECT No. J76-22-02

FIGURE No. 2

Cadd FILE No.



INDIAN ORCHARD BROWNFIELDS SITE

SPRINGFIELD, MASSACHUSETTS

PROPOSED BORING LOCATIONS PINEVALE STREET PROPERTY

SCALE IN FEET

1"= 60'

0' 30' 60' 120'

DESIGNED BY: JEG DRAWN BY: CDA
REVIEWED BY: DJM DATE: DEC. 5, 2000
REV: OCTOBER 2002/ CDA

O'REILLY, TALBOT & OKUN ASSOCIATES, Inc.

PROJECT No. J76-22-02

FIGURE No. 3

Appendix A

APPENDIX A
LABORATORY INFORMATION (SOPs, MDL STUDIES)

AMRO Environmental Laboratories Corporation

111 Herrick Street, Merrimack, NH 03054
TEL: (603) 424-2022 · FAX: (603) 429-8496

VOLATILE ORGANICS ANALYSIS

SW-846 METHOD 8260B

Procedure Number: OL-2001

Revision No.: 6

Revision Date: 07/06/2001

Prepared By: _____ Date: 7/6/01

Approved By: _____ Date: 7/6/01
VOA Supervisor

Approved By: _____ Date: 7/6/01
Organic Manager

Approved By: _____ Date: 7/6/01
Laboratory Director

Approved By: _____ Date: 07/06/2001
Quality Assurance Manager

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1.0 SCOPE and APPLICATION

This procedure details the steps taken by AMRO Environmental Laboratories Corporation to produce accurate and reliable results for volatile organic analyses using Method 8260B, Rev. 2 12/96 from the SW-846 Manual.

Method 8260B is used to determine volatile organic compounds in ground and surface water, aqueous sludges, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

The following lists of compounds are analyzed by purge and trap GC/MS using a 5mL aliquot of sample:

TABLE 1

CAS. NO.	COMPOUND	WATER REPORTING LIMITS (µg/L)	MEDIUM LEVEL SOILS REPORTING LIMITS (µg/Kg)	LOW LEVEL SOILS REPORTING LIMITS (µg/Kg)
75-71-8	Dichlorodifluoromethane	5	50	5
74-87-3	Chloromethane	5	50	5
75-01-4	Vinyl chloride	2	25	5
75-00-3	Chloroethane	5	50	5
74-83-9	Bromomethane	2	50	5
75-69-4	Trichlorofluoromethane	2	50	5
60297	Diethyl ether	10	250	25
74-88-4	Idomethane	2	25	5
67-64-1	Acetone	10	250	50
75-35-4	1,1-Dichloroethene	1	25	5
75-15-0	Carbon disulfide	2	50	5
75-09-2	Methylene chloride	5	50	25
107-02-8	Acrolein	75	N/A	N/A
107-13-1	Acrylonitrile	10	N/A	N/A
1634-04-4	Methyl tert-butyl ether	2	25	5
156-60-5	trans-1,2-Dichloroethene	2	25	5
75650	tertiary Butanol	100	2500	100
75-34-4	1,1-Dichloroethane	2	25	5
108-20-3	Diisopropyl ether	2	25	5
109-05-4	Vinyl acetate	10	N/A	N/A
637-92-3	Ethyl tertiary butyl ether	2	25	5
78-93-3	2-Butanone	10	250	25
594-20-7	2,2-Dichloropropane	2	25	5
156-59-2	cis-1,2-Dichloroethene	2	25	5

CAS. NO.	COMPOUND	WATER REPORTING LIMITS (µg/L)	MEDIUM LEVEL SOILS REPORTING LIMITS (µg/Kg)	LOW LEVEL SOILS REPORTING LIMITS (µg/Kg)
67-66-3	Chloroform	2	25	5
74-97-5	Bromochloromethane	2	25	5
71-55-6	1,1,1-Trichloroethane	2	25	5
56-23-5	Carbon tetrachloride	2	25	5
107-06-2	1,2-Dichloroethane	2	25	5
71-43-2	Benzene	1	25	5
994-05-8	Tertiary amyl methyl ether	2	25	5
109999	Tetrahydrofuran	10	250	25
79-01-6	Trichlororethene	2	25	5
78-87-5	1,2-Dichloropropane	2	25	5
75-27-4	Bromodichloromethane	2	25	5
74-95-3	Dibromomethane	2	25	5
108-10-1	4-Methyl-2-pentanone	10	250	25
10061-01-5	cis-1,3-Dichloropropene	1	25	5
108-88-3	Toluene	2	25	5
10061-02-6	trans-1,3-Dichloropropene	2	25	5
79-00-5	1,1,2-Trichloroethane	2	25	5
106-93-4	1,2-Dibromoethane	2	25	5
110-75-8	2-Chloroethyl-vinyl-ether	10	N/A	N/A
591-78-6	2-Hexanone	10	250	25
142-28-9	1,3-Dichloropropane	10	25	5
127-18-4	Tetrachloroethene	2	25	5
124-48-1	Dibromochloromethane	2	25	5
108-90-7	Chlorobenzene	2	25	5
670	1,1,1,2-Tetrachloroethane	2	25	5
100-41-4	Ethylbenzene	2	25	5
108-38-3	m-Xylene	2	25	5
106-42-3	p-Xylene	2	25	5
95-47-6	o-Xylene	2	25	5
100-42-5	Styrene	2	25	5
75-25-2	Bromoform	2	25	5
98-82-8	Isopropylbenzene	2	25	5
79-34-5	1,1,2,2-Tetrachloroethane	2	25	5
96-18-4	1,2,3-Trichloropropane	2	25	5
108-86-1	Bromobenzene	2	25	5
103-65-1	n-Propylbenzene	2	25	5
95-49-8	2-Chlorotoluene	2	25	5
106-43-4	4-Chlorotoluene	2	25	5
108-67-8	1,3,5-Trimethylbenzene	2	25	5

CAS. NO.	COMPOUND	WATER REPORTING LIMITS (µg/L)	MEDIUM LEVEL SOILS REPORTING LIMITS (µg/Kg)	LOW LEVEL SOILS REPORTING LIMITS (µg/Kg)
98-06-6	tert-Butylbenzene	2	25	5
95-63-6	1,2,4-Trimethylbenzene	2	25	5
135-98-8	sec-Butylbenzene	2	25	5
99-87-6	4-Isopropyltoluene	2	25	5
541-73-1	1,3-Dichlorobenzene	2	25	5
106-46-7	1,4-Dichlorobenzene	2	25	5
104-51-8	n-Butylbenzene	2	25	5
95-50-1	1,2-Dichlorobenzene	2	25	5
96-12-8	1,2-Dibromo-3-chloropropane	5	50	5
120-82-1	1,2,4-Trichlorobenzene	2	25	5
87-68-3	Hexachlorobutadiene	2	25	5
91-20-3	Naphthalene	5	50	5
87-61-6	1,2,3-Trichlorobenzene	2	25	5

2.0 METHOD SUMMARY

2.1 Samples are introduced to the GC/MS System by directly placing the VOA vials into the autosampler tray. Standards are prepared in volumetrics and transferred to 40mL VOA vials. The autosampler syringe delivers 5mL to the purging chamber along with the internal standards and surrogates (the autosampler is equipped with a syringe or vial, which the operator fills with the internal standard and surrogate mix for waters and internal standard mix for soils). Also, a 40mL VOA vial containing Bromofluorobenzne (BFB) at a concentration of 50ng/5mL is placed on the tray for tuning (no SS is added).

2.2 Helium purges through the chamber and the volatile analytes are absorbed on the trap, a tube containing an OV-1/Tenax/Silica Gel/Charcoal mixture. After purging is complete, the trap is heated and backflushed with helium to desorb the compounds. The analytes are carried along a heated transfer line to the GC inlet, where the glass liner meets the narrow bore capillary column. At this point the analytes are heated, mixed and split. The column is temperature programmed to separate the analytes and is interfaced by a Mass Spectrometer for detection.

2.3 Identification of target analytes is accomplished by comparing their mass spectra with that of standards. Quantitation is done by comparing the response of a major ion relative to that of an internal standard using from 8 to 10 point calibration curve.

2.2 The GC/MS operators should be thoroughly trained and skilled in the use of purge and trap GC/MS before being authorized to analyze and report sample results independently. All analysts shall complete Qualification Card for SW-846 Method 8260B, see Attachment 1.

2.3 Method Modification – The compounds listed above include the 8260 compounds. AMRO has demonstrated that the additional analytes are achievable through initial demonstration of capability.

3.0 DEFINITIONS

3.1 **Method Blank:** An aliquot of reagent water, which is carried through the entire analytical procedure with the samples, its purpose is to determine whether contamination is present during the analysis. A method blank is analyzed 1 for every analytical batch of samples.

3.2 **Laboratory Control Sample:** An aliquot of reagent water which known quantities of the method analyte are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine the degree to which the analytical result approaches the "true value" of the concentration of the analyte being determined. The percentage recovery is calculated in order to assess the efficiency of the analysis.
One (1) LCS is analyzed for every analytical batch of samples.

3.3 **Sample Duplicate:** A duplicate is analyzed for every 20 samples in the form of a Matrix Spike/Matrix Spike Duplicate to verify the method precision.

3.4 **Matrix Spike:** A specific aliquot of sample into which a known amount of analyte is added. The analytical spike is analyzed with the sample batch and the percent recovery is calculated in order to assess the matrix effect on the analytical system.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

4.1 All samples must be iced or refrigerated at $4^{o}C \pm 2^{o}C$ from the time of collection until analysis.

4.2 Aqueous sample collection is done by our clients using 40mL pre-washed and pre- preserved glass vials. The sampler is instructed to fill the vial so it is completely full to the point of a positive meniscus but not overflowing without any air bubbles. A Teflon-sealed cap is then screwed tight onto the vial. The vial is inverted to insure that there are no air bubbles. A triplicate sampling is always done so that another vial of the same sample is available for analysis in case one of the following occurs:

A. The sample dilution has to be made.
B. There's an air bubble in the vial
C. The vial is broken in transport.

4.3 All aqueous samples **must** be analyzed within 14 days of collection and **should** be field preserved with 1:1 HCl to a pH<2.

4.4 All aqueous samples are pH checked after analysis. The pH results are documented in the injection run logs for each sample. All samples analyzed

using EPA Method 624 that have a pH of > 2 must be analyzed within 7 days of collection. If this un-preserved holding time is exceeded, the data is to be flagged and this information is included on the final report. All samples analyzed using SW-846 Method 8260B must have a pH<2. If none of the sample vials have a pH<2, the data is flagged and noted in the case narrative.

4.4.1 If samples are suspected to contain Residual Chlorine, 10 mg of Sodium Thiosulfate must be added to each 40mL VOA vial at time of sampling.

4.5 Sample Compositing Procedure: The following method is used upon client request to prepare a composite of wastewater volatile samples for analysis.

4.5.1 Check the chain-of-custody to determine if the flow rates are equal or unequal.
4.5.2 The sample vials are stored in the refrigerator banded together.
4.5.3 If flows are ***equal***, pour the entire contents of all the VOA vials that need to be composited into an appropriate size Erlenmeyer flask (250 or 500 mL).
4.5.4 Swirl the flask **gently** so as not to release the volatile compounds of the samples.

4.5.5 **Gently** pour the sample back into vials and tightly screw on Teflon-lined septa caps.
4.5.6 Label the vials with the appropriate project number and sample ID (comp).
4.5.7 Always prepare at least two vials of a composite.
4.5.8 If flow rates are ***unequal***, the client provides the amounts of sample needed of each sample vial to prepare the composite.
4.5.9 Using a graduated cylinder or gas-tight syringes, measure out the exact amount needed from each sample portion and gently pour into an Erlenmeyer flask.

4.6 Continue by following procedure steps 4.5.4 through 4.5.7.

4.7 Compositing of aqueous samples other than wastewater must be analyzed separately and the results averaged.

4.8 Store samples at 4°C until needed for analysis.

4.9 8260/5035 and VPH Methanol Soil Sample Preparation:

20mL of purge and trap grade methanol is measured out into VOA vials, spiked with 40µL of a VOA surrogate mix at 1,250 ng/µL, weighed, recorded and sent out for sample collection. The VOA vials are returned with about 20g

of soil in each sample vial. One methanol vial is sent out as a trip blank with each project.

4.10 Methanol Soil Collection for the State of New Jersey:

4.10.1 25 mL of purge and trap methanol are measured into VOA vials, spiked with 25µL of VOA surrogate spike mix at a concentration of 2,500ng/µL, and sent out for sample collection. One is sent as methanol trip blank. The VOA vials are returned with approximately 10g of soil in each sample vial.

4.11 EnCore Sampler Procedure:

EnCore samplers containing soil samples have a 48 hour holding time. When EnCore samplers are received from the field, two sodium bisulfate vials and one methanol vial are prepared. Using the EnCore Extrusion tool, remove the soil from each EnCore sampler and place into a vial prepared with sodium bisulfate. Repeat the procedure for another prepared sodium bisulfate vial. Remove a soil aliquot from another EnCore sampler and place into a prepared methanol vial. These vials are used for extraction and analysis. The 14 day hold time for soil samples begins at the time of collection, not the time of preservation.

3.8.1 Methanol Vials: 10mL of purge and trap grade methanol is measured out into VOA vials, spiked with 20µL of a VOA surrogate mix at 1,250 ng/µL, weighed and recorded in the EnCore soil prep log.

3.8.2 Sodium Bisulfate Vials: 5mL of VOA reagent water and 1.0g of sodium bisulfate is added to a VOA vial, weighed and recorded into the Sodium Bisulfate preparation logbook. Vials may be purchased pre-prepared from Sci/Spec (cat # 276740-5SBST). Representative samples must be tested for each lot to ensure target analytes are not present in the bisulfate solution. One NaHSO4 vial is sent out as a trip blank with each project.

5.0 POTENTIAL PROBLEMS AND INTERFERENCES

It is important to be able to demonstrate that analytical results are not biased by laboratory contamination. The GC/MS operator is responsible for taking the following precautions.

5.1 GLASSWARE and SYRINGES:

5.1.1 All glassware and syringes used in the preparation of volatile organic standards or samples are thoroughly cleaned before each use.

5.1.2 Syringes for transferring methanol based standards are rinsed with methanol a minimum of three times before each use. Syringes for samples and aqueous standards are rinsed with methanol and then three times with distilled volatile-free water before each use.

5.1.3 Volumetric flasks and other glassware used in the preparation of samples or standards are rinsed with methanol and then three times with distilled water for aqueous based samples and standards or three times with methanol for methanol standards.

5.2 PURGE and TRAP UNITS Tekmar LSC 2000,Tekmar LSC 3000, O-I 4560, and Dynatech Dynatrap

The Purge and trap unit can be a source of contamination in volatile organic samples.
To minimize the possibility of this occurring, the following steps are taken.

5.2.1 The Tekmar LSC 2000, 3000 and autosampler automatically drains the sample out after purging and bakes out the trap at 225°C for 8 minutes while purging helium through the purging chamber. The autosampler rinses its syringe with distilled water and also flushes the purge lines and purge chamber twice during the bake cycle.

5.2.2 The sample analyses are examined before running the instrument the next day. If a sample contains high amounts of analytes, the next sample is examined to see if it contains any of the analytes. If there is any possibility of analytes carrying over from the previous sample, the sample(s) following are re-analyzed.

5.2.3 Method blanks are analyzed daily and must meet acceptance criteria before samples are analyzed.

5.2.4 Occasionally, the purging chamber is cleaned with soap and water and then rinsed.

5.3 CONTAMINATION FROM OTHER SOURCES:

5.3.1 Special precautions are taken for Methylene Chloride and Acetone contamination. The analytical and sample storage area is isolated from the extraction lab. All carrier gas lines and purge gas plumbing are made of copper or stainless steel tubing. The volatile lab is isolated in a separate room. Occasionally Methylene Chloride will show up in water blanks or methanol blanks, rarely above 5ppb. All data must be flagged if the level of Methylene Chloride exceeds the reporting level.

5.3.2 Trip blanks are analyzed with samples to check for contamination. Trip blanks are provided by AMRO and are analyzed to check for contamination by diffusion of volatile organics through the septum seal of the sample container into the sample during shipment and storage.

5.3.3 Volatile organic sampling vials may be contaminated. Vials supplied by AMRO have been purchased pre-cleaned from a reputable supplier that uses the EPA protocol to clean their vials. AMRO policy does not allow re-use of volatile organic sampling vials.

5.3.4 Refrigerator blanks are used to determine contamination of the refrigerators. Refrigerator Water and Methanol blanks are analyzed monthly and evaluated to determine if there are any analytes detected that exceed the reporting limits. Any hits are investigated to determine the source of the contamination. Data will be reviewed by QC and kept on file by the VOA department.

5.4 MATRIX INTERFERENCE

5.4.1 Sometimes, when a sample is analyzed, it foams, or contains compounds that interfere with the internal standards or surrogates. Such a sample is not re-analyzed due to potential harm to the instruments. It is considered to be due to matrix interference and the data is flagged and listed in the case narrative.

6.0 HEALTH AND SAFETY

6.1 AMRO has a laboratory safety program in place that applies to all employees. There is a safety officer as well as employees with 40 hours of OSHA training. The air quality of the laboratory has been monitored and employees are sent for physicals. All employees receive fire and safety training upon employment.

6.2 Fire extinguishers are located in various areas of the lab. A lab evacuation plan is posted in every room, with a designated meeting place.

6.3 All new analysts receive training on the safe handling of samples, standards, the changing of gas cylinders, and the operation of instruments. In the lab, clean laboratory coats and gloves are worn when working with samples. Neat standards are made up in hoods. When gas tanks are replaced, the carrier with chain is used properly, and all gas tanks are chained in place. Soap is used to check for any leaks.

6.4 Care is taken with glassware and syringes to prevent injury. Broken glass and syringes are promptly removed to broken glass containers. First aid kits are available throughout the lab. There are also eyewash stations and an emergency shower.

6.5 MSDS's are reviewed for each chemical used to ensure proper precautions are observed when handling chemicals.

6.6 Pollution prevention – The use of chemical exhaust hood are required when working with chemicals. They are specifically designed to minimize analyst exposure. The hood exhaust is monitored periodically to ensure environmental exposure is minimized.

6.7 Waste control – AMRO takes whatever steps possible to minimize waste. This includes volume reduction where appropriate. AMRO also properly segregates wastes according to contaminants and a commercial vendor is utilized for waste disposal.

7.0 INSTRUMENTS AND EQUIPMENT

7.1 SW-846 Method 8260B is performed on Hewlett Packard 5890 and 6890 Gas Chromatographs with 5971, 5972 and 5973 Mass Selective Detectors. They are equipped with purge and trap units, auto samplers, and data systems with the following software: Hewlett Packard DOS Chemstation for data acquisition, and Enviroquant for data processing, including the NBS 54K Library or NIST 74K Library of Mass Spectra. Columns used for each instrument are listed in section 9.1.

7.2 Edwards Vacuum Pump

7.3 Balance: Analytical 0.0001g

7.4 Gas Tight Syringes: 10, 25, 50, 100, 250, 500, 1,000uL, 5, 10, or 25 mL with manufacturer tolerances of ±1%.

7.5 Class A volumetric flasks: 1, 2, 5, 10, 25, 50, 100, 250, 500, &1,000mL

7.6 Stainless steel spatulas.

7.7 Glass disposable pipets.

7.8 Pre-cleaned 40mL VOA vials with Teflon Septum and screw caps.

8.0 REAGENTS AND STANDARDS

8.1 AMRO VOA reagent water – Reverse Osmosis/Granular Activated Carbon (RO/GAC) Water from a Culligan System. Method Blanks are used to monitor contaminant levels of volatile analytes. Reagent water is used for making up daily standards, dilutions, water blanks, and rinsing flasks and syringes.

8.2 Methanol, purge and trap grade, from Fisher Scientific or Burdick and Jackson is used for making up standards and rinsing syringes.

8.3 1:1 Hydrochloric Acid (HCl) for preservation.

8.4 Sodium Thiosulfate (ACS) Granular – purchased from Fisher Scientific. Refer to sample receipt SOP for more information.

8.5 Sodium Bisulfate (ACS) Granular from Fisher Scientific.

8.6 Stock solutions of standards

8.5.1 Both stock and working standards in methanol are stored in the freezer. Daily standards are made up in water, stored without headspace, and are discarded after each day of use.

8.5.2 Occasionally, clients may ask for additional compounds, which may be purchased and analyzed to provide a semi-**quantitative result that would be considered estimated.** Complete method start-up and initial demonstration of proficiency is required for all new analytes reported without qualifiers.

8.5.3 Good laboratory procedure for making up standards is as follows:

8.5.3.1 All syringes and volumetric flasks are rinsed three times with methanol.

8.5.3.2 Syringe needles are wiped with Kimwipes and air dried by pumping the plunger up and down several times.

8.5.3.3 The volumetric flask is filled with methanol as high as possible, leaving room for the addition of the standard.

8.5.3.4 The standard is drawn up in the syringe above the desired level, inverted to allow any air bubble to rise to the needle, and the plunger is pushed to the correct amount.

8.5.3.5 The needle is wiped with a Kimwipe and the needle is placed into the flask, preferably under the methanol and the plunger is pushed down gently to avoid purging.

8.5.3.6 If the needle can not reach the methanol, even with tilting the flask, then it should be eluted slowly down the side of the glass.

8.5.4 Initial and CCV calibration stock standards: Used within six months after ampule opening unless otherwise indicated:

8.5.4.1 502/524 MegaMix obtained from Supelco at 2,000µg/mL in Methanol. Refer to Attachment 3.

8.5.4.2 VOC MIX #6 obtained from Supelco at concentration 2,000µg/mL is used for calibration. Ampule used weekly. Refer to Attachment 4.

8.5.4.3 Restek Custom VOA Mix #1: Used for Calibration

Compound	Concentration (µg/mL)
Acetone	2,000
2-Butanone	2,000
2-Hexanone	2,000
Methyl tert-butyl ether	2,000
2-Methyl-2-pentanone	2,000

Compound	Concentration (µg/mL)
Tetrahydrofuran	2,000
Diethyl ether	2,000
Cyclohexanone	20,000

8.5.4.4 Restek Custom VOA Mix #2: Used for Calibration

Compound	Concentration (µg/mL)
Carbon Disulfide	2,000
1,1,2-Trichlorotrifluoroethane	2,000
Dichlorofluoromethane	2,000
Methylmethacrylate	2,000
2-Chloroethylvinyl ether	2,000
Acrylonitrile	2,000
Iodomethane	2,000

Restek Custom Oxygenates Standard: Used for Calibration

Compound	Concentration (µg/mL)
Diisopropyl ether	2,000
Tertiary amyl methyl ether	2,000
Tertiary Butanol	20,000
Ethyl tertiary butyl ether	2,000

8.5.4.5 Acrolein obtained from Restek 20,000 µg/mL used for Calibration.

8.5.4.6 Vinyl Acetate obtained from Restek 2,000 µg/mL used for Calibration.

8.5.5 Stock Quality Control check standards (used for LCS): Used within six months after ampule opening unless otherwise indicated.

8.5.5.1 CAL MIX 2000 obtained from Restek at 2,000µg/mL. Refer to Attachments 5A and 5B.

8.5.5.2 CAL MIX #1 obtained from Restek, concentration 2,000µg/mL. Used from calibration verification. Good for one month after opening. Refer to Attachment 6.

8.5.5.3 8260 Ketone Mix obtained from ECS at 2,000µg/mL containing Acetone, 2-Butanone, 2-Hexanone, 2-Methyl-2-pentanone.

8.5.5.4 8260 Add Ons Mix obtained from ECS at 2,000 ug/mL containing Carbon Disulfide, Vinyl Acetate, Iodomethane and Methyl-tert-butyl ether (MTBE).

8.5.5.5 New Hampshire Oxgenates Mix from ECS at 2,000 ug/mL containing Ethyl tertiary butyl ether, Diisopropyl ether, Tertiary amyl methyl ether, and at 20,000 ug/mL, tertiary Butanol..

8.5.5.6 Diethyl Ether and Tetrahydrofuran are obtained from Chem. Service and are prepared from neat.

8.5.5.7 8260A Internal Standard obtained from Restek, contains Fluorobenzene, Chlorobenzene-d5, 1,4 Dichlorobenzene-d4 at 2,500 ng/µL.

8.5.5.8 8260A surrogate solution is obtained from Restek and contains 1,2-Dichloroethane-d4, Toluene-d8, p-Bromofluorobenzene, Dibromofluoromethane at 2,500 ng/µL.

8.5.5.9 4-Bromofluorobenzene (BFB) obtained from Supelco at concentration 2,000 ng/µL used to tune instruments. Used within three months.

8.5.6 Working standards - good for one week unless otherwise indicated.

8.5.6.1 Initial and daily calibration working standards mix. Combine the following stock mixes into one 5mL volumetric flask and transfer to a 5mL vial with a septum cap. Store in the freezer at all times.

8.5.6.1.1 502/504 MegaMix – 250 µL of Stock to 5 mL final volume with Methanol for a final concentration of 100 ng/µL.

8.5.6.1.2 VOC mix #6: 250uL of stock to 5 mL in methanol, final concentration.100ng/µL.

8.5.6.1.3 Custom VOA Mix #1 – 250 µL of Stock to 5 mL final volume with Methanol for a final concentration of 100 ng/µL.

8.5.6.1.4 Custom VOA Mix #2 – 250 µL Stock to 5 mL final volume with Methanol for a final concentration of 100 ng/µL.

8.5.6.1.5 Custom Oxygenates Standard Mix—250uL Stock to 5 mL final volume with Methanol for a final concentration of 100 ng/µL.

8.5.6.1.6 Acrolein – 250 µL of stock to 5mL final volume in methanol for a final concentration of 1000 ng/µL.

8.5.6.1.7 Vinyl Acetate – 250 µL of Stock to 5 mL final volume with Methanol for a final concentration of 100 ng/µL.

8.5.6.2 Quality control check standards (LCS)– good one month unless otherwise specified.

8.5.6.2.1 CAL Mix #1: 25uL of stock Cal Mix #1 to 5mL final volume in Methanol for a final concentration of 10ng/µL. Good one week.

8.5.6.2.2 CAL Mix – consists of the following:

8.5.6.2.2.1 CAL MIX 2000 – 125 uL of Stock to 25mL final volume with Methanol for a final concentration of 10 ng/µL.

8.5.6.2.2.2 8260 Ketone Mix - 125uL stock to 25mL final volume in methanol for a final concentration of 10ng/µL.

8.5.6.2.2.3 8260 Add Ons Mix – 125µL of Stock to 25mL final volume with Methanol for a final concentration of 10ng/µL.

8.5.6.2.2.4 NH Oxygenates Mix – 125µL of Stock to 25mL final volume with Methanol for a final concentration of 10ng/uL.

8.5.6.2.3 IS/Surrogate solution

Instrument V1a
480 µL of 8260 IS Mix to 10 mL in methanol. Final concentration 120ng/µL.

Instrument V2
500uL of 8260 IS Mix to 10 mL in methanol. Final concentration 125ng/µL.

Instrument V3
360uL of 8260 IS Mix and 8260 SS Mix to 10 mL in methanol. Final concentration 90ng/µL.

Instrument V4
Soil - 480uL of 8260 IS Mix to 10 mL in methanol. Final concentration 120ng/µL.
Water – 400uL of 8260 IS Mix and 8260 SS Mix to 10mL in methanol. Final concentration 100ng/µL.

8.5.6.3 BFB

8.5.6.3.1 125µL stock to 10 mL in methanol, final concentration 25ng/µL.

8.5.6.4 Surrogate calibration working solution

8.5.6.4.1 500µL of Restek 8260A surrogate stock solution plus 250µL of Accustandard DBT stock solution into 5mL of methanol, for a final concentration of 250µg/mL

8.5.7 Daily Standards are made up daily in VOA reagent water. All standards for extracted soil calibration or calibration verification are made in reagent water with 4% methanol added. Surrogates and Internal Standards are added by the autosampler for all water and low level soil standards.

8.5.7.1 Initial calibration standards:

8.5.7.1.1 0.5, 1, 2, 5, 10, and 25µL of the combined working solution, plus 40uL of the surrogate calibration working solution when calibrating for soils, into 100mL of reagent water to prepare the 0.5, 1, 2, 5, 10, and 25µg/L aqueous and soil standards, respectively. To prepare the 50, 100, 200, and 300 µg/L aqueous standards, add 25, 50, 100, and 150µL of the combined working solution, plus 15, 10, 5, and 2µL respectively of the surrogate calibration working solution when calibrating for soils, into 50mL of reagent water. For low soils; 5mls of 5, 10, 25, 50, 100, 200, and 300ug/L standard is transferred to VOA vial containing 5g of sand.

8.5.7.2 Daily calibration verification standards

8.5.7.2.1 LCS: 100µL Cal Mix solutions to 50 mL DI, and Cal Mix #1, 100 µL to 50 mL DI, for a final concentration 20µg/L.

8.5.7.2.2 BFB: 40µL working standard solution to 100 mL DI, final concentration 10ng/mL.

8.5.8 Tracking of Analytical Standards

8.5.8.1 Chemical Receipt

The receipt of all standards, neat compounds and reagents from commercial sources is documented in the Chemical Receiving Logbook by sample receiving personnel or designate. Each solution or compound is assigned a unique standard receipt ID number, the letter "A" and a four digit sequential number. The date received, source, lot number, expiration date and disposal date are recorded. The expiration dates are provided from the manufacturer and the disposal dates are completed by AMRO employees when standards are used up or disposed.

8.5.8.2 Standards Preparation

Standards are prepared as written in the respective SOPs. In order to assure the accuracy of standards the following general guidelines are used:

8.5.8.2.1 AMRO purchases pesticide residue grade solvents and purge and trap grade Methanol for organic standard preparation and organic sample extractions.

8.5.8.2.2 ACS reagent grade chemicals are used when the method warrants.

8.5.8.2.3 Any stock standards that are purchased are accompanied by a certificate of analysis from the manufacturer.

8.5.8.2.4 Class A volumetric glassware is used to prepare standards.

8.5.8.3 Standard Tracking

It is important to be able to track all analytical standards back to their sources. The following procedure is used by AMRO personnel to accomplish this:

Organic Standard Tracking - The Organic Standards Tracking Log consists of three sections plus an ID index. The ID index assures that no two standards are assigned the same ID number.

8.5.8.3.1 Stock Section - Whenever a stock standard solution is opened or is prepared from a neat compound, this information is recorded in the Stock Standard Logbook section of the standard tracking log . The stock solution is assigned a new ID number consisting of the date of preparation plus a letter suffix starting with the letter "A". This ID along with the compound name, concentration and initials of the person making the stock are included on the label. Stock standards are good one year from the date prepared or the date provided by manufacturer, whichever is shorter. Example - The fourth volatile standard prepared on April 15, 1989 would have the standard ID V041589D. This number will be recorded in the logbook and written on the container.

8.5.8.3.2 Working Section - Whenever a working standard solution opened or is prepared, whether from AMRO stocks or commercially obtained stocks, the information is recorded in the Working Standard section of the standard tracking log. The solution is assigned a new ID number based on the date it is prepared plus a letter suffix. This number along with a descriptive name, concentration (or conc. varied) and the initials of the person preparing the solution are included on the label. The expiration of working standards vary depending on the use. Standards should be used in accordance with method specifications and manufacturer's instructions.

8.5.8.4 Standard Storage - Standards and reagents are stored per method specifications and manufacturer's instructions. Volatile standards are stored in a freezer at minus 10°C to 20°C.

8.5.8.5 Solvent Check Analysis

All extraction procedures are performed using pesticide residue grade solvents and a method or procedural blank analysis is performed when a new lot number is received to verify the absence of target analytes.

9.0 GC/MS PROCEDURE

9.1 Instrument Conditions and Settings

9.1.1 GC/MS (V-1A): HP-624 25 m x 0.2 mm ID column 35 ° C for 5 min., 8 ° C/min to 195 ° C, hold for 4 min. for a total of 29 min. analyzed time Tekmar LSC 3000 purge and trap Dynatech PTA-30w/s Autosampler Supelco Trap E

9.1.2 GC/MS (V-2): HP-624 25m x 0.2mm ID column 35 ° C for 5 min., 8 ° C/min to 195 ° C, hold for 4 min. for a total of 29 min. analyzed time
Tekmar LSC 2000 purge and trap Dynatech Archon w/s autosampler.
Supelco Trap E

9.1.3 GC/MS (V-3): HP-624 25m x 0.2mm ID column 35°C for 5 min., 8°C/min to 195°C, hold for 4 min. for a total of 29 mins analyzed time
Dynatrap Purge Trap E Dynatech Precision Sampling Dynatrap Autosampler.

9.1.4 GC/MS (V-4): RTX-624 20m x 0.18 mm ID column35°C for 4 min., 10°C /min to 195 °C, hold for 3 min. for a total of 23 min. analyzed time. 4560 OI Sample Concentrator and Archon autosampler.

9.1.5 All systems have a capillary injection port, operating in the split mode.

9.1.6 V1A, V3 and V4 have Water Management Systems with a 150°C Bake, 100°C Purge and 50°C Desorb.

9.1.7 Settings:

Purge gas - helium grade 99.995
Purge time - 11 minutes
Purge flow - 25-30 mL/min
Desorb Flow - 30 mL/min
Desorb Time - 4 min at 200°C
Bake Time - 8 min at 225°C
Tekmar valve and transfer line temp - 105°C
Injection port temp - 225°C
Detector temp - 160-180°C
Transfer line temp - 280°C
Split Ratio 30:1

Purge temp. – ambient for all Dynatrap/Tekmar 2000 AS. 25°C for V4 (O.T. 4560), and 40°C for all low level bisulfate preserved soils.

V-4 has an Electronic Pressure Control – constant flow 0.5 mL/min.

9.2 Initial Demonstration of Capabilities

It is important to be able to demonstrate that all sample analyses were performed in an 'in-control' manner. It is the responsibility of the GC/MS operator to perform the following procedures prior to sample analysis.

9.2.1 Initial Demonstration of Lab Performance

The ability of AMRO to produce accurate and precise data is demonstrated per instrument/per analyst for each method. This information was entered on an Excel® spreadsheet and is kept on file with the QC department along with the associated chromatograms and quantitation output pages. It consists of an Initial Calibration (IC) for all target analytes, Initial Calibration Verification (ICV) for all target analytes, a Method Detection Limit Study (MDL) and Precision and Accuracy Study (P&A) for each analyte, each instrument and each matrix on an annual basis.

9.2.2 MDL

The method detection limit is defined in 40 CFR 136 Appendix B. The MDL is determined annually by the analysis of a minimum of seven replicate samples, all containing an analyte(s) of the same low-level concentration. These replicate samples are put through all the preparation steps that a sample is put through. The standard deviation of the results of these analyses is multiplied by the appropriate student T-test value and the resulting value is deemed the method detection limit for that specific analyte.

MDL studies of each analyte must be reported annually for each instrument, column, matrix, and extraction method. To ensure that reasonable MDL values are determined, an MDL check sample is analyzed by spiking an interference free matrix with all target analytes at about two times the determined MDL. The MDL check sample is taken through the same process as the MDL. If any of the target analytes are not detected, the MDL study is modified and repeated until the MDL check sample is detectable. The MDL check will be analyzed quarterly and after major instrument maintenance or changes in the instrumentation or instrumental conditions to verify sensitivity of the method.

9.2.3 Precision &Accuracy

Accuracy is a measure of the degree to which the analytical result approaches the "true" value of the concentration of the analyte being determined. Precision in the laboratory is determined by the comparison of duplicates, where duplicate samples result from an original sample that has been split for identical analyses. Precision and Accuracy in the laboratory is assessed initially by the analyses of a minimum of 4 replicate samples at a mid-level point of the expected range. The percent recoveries and Relative Standard Deviations (RSD) are evaluated and compared to method specifications or default limits where applicable.

The regular analysis of known standards such as the Laboratory Control Samples (LCS), and matrix and analytical spikes also assess accuracy. Accuracy within the laboratory is expressed in terms of percent recovery.

The precision of data is regularly evaluated by determining the relative percent difference (RPD) of duplicate (replicate) analyses.

9.3 Tuning

The mass spectrometer must be verified to be in tune, has adequate sensitivity, is standardizing for the compounds of interest, and is demonstrating that the system is free of interferences. Calibration begins with the analysis of Bromofluorobenzene (BFB). This performance test must be passed before any samples, blanks, or standards are analyzed. The calibration is good for 12 hrs from the injection time of the BFB for 8260B.

9.3.1 **Tuning** - 50 ng of BFB (40 µL of a 25ng/µL solution) is added to 100 mL of VOA free water. 5 mL is purged for 11 minutes and desorbed onto the chromatographic column. The analysis is performed at 100° C to 150° C. A scan delay of two to five minutes is used. After the scan delay, data is acquired for five to ten minutes. The expected elution time of the BFB is six to eight minutes from the start of data acquisition. The background corrected average of three scans at the apex or of the entire peak of the peak is checked against the tuning requirements in Table 1. One simple subtraction of background is required within twenty scans of the left side of the peak. There is a procedure file program in the software that will locate and check the BFB for a passing spectrum in the manner explained above. This procedure will be used routinely to eliminate any subjectivity from the tuning process. If this procedure fails to produce ion abundances that meet the criteria, it will display the message "no passing spectrum found in data file: xxxxx" on the

printer. If this occurs the BFB must be re-analyzed. If repeated analyses fail to produce acceptable results, then the instrument must be manually tuned according to the Hewlett-Packard reference manual. If the tune does not meet criteria, a single scan option can be used. This should not be required on a routine basis. If it does become necessary, consult with the section head. Once an acceptable tune is obtained, the following items are documented in the analyzed log:

9.3.1.1 The scan number(s) of the good tune and background corrections used to achieve it.

9.3.1.2 The time of injection.

9.3.1.3 Once a good spectrum is found a hardcopy of the following information is filed in the daily calibration file.

9.3.1.4 The following is the BFB tune criteria:

Table 2
BFB Mass - Intensity Specifications

Mass	Intensity Required (relative abundance)
50	15 to 40% of Mass 95
75	30 to 60% of Mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of Mass 95
173	Less than 2% of Mass 174
174	Greater than 50% of Mass 95
175	5 to 9% of Mass 174
176	Greater than 95% but less than 101% of Mass 174
177	5 to 9% of Mass 176

9.4 Initial Calibration Procedure

A multi-level calibration consisting of 0.5, 1, 2, 5, 10, 25, 50, 100, 200, 300 ug/l is performed using standards obtained commercially. The three internal standards that are used: Fluorobenzene, Chlorobenzene-d5, and 1,4 Dichlorobenzene-d4 at a level of 25.0 ug/L.

9.4.1 The RRF (Relative Response Factor) is calculated as follows:

$$RRF = \frac{(Ax \times Cis)}{(Ais \times Cx)}$$

where: Ax = Area of the characteristic ion for the compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cis = Concentration of the specific internal standard.
Cx = Concentration of the compound being measured.

The average RRF and % Relative Standard Deviation (%RSD) must be calculated for each compound using the 8-10 RRF values calculated for each compound from the initial (8-10 point) calibration curve.

If the % RSD of any compound is less than or equal to 15%, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation. See Table 2 for analyte list and criteria.

If the % RSD of any compound is 15% or greater, construct calibration curves of area ratio (A / Ais) versus concentration ratio (Cx/ Cis) using first order (Linear Regression) or second order (Quadratic Regression) regression fit of the initial calibration points. The requirement for Linear Regression correlation coefficient is greater than 0.990. If the Linear Regression criteria is not met, then Quadratic equation (second order) may be used with a minimum of 6 data points. In either case, the curve must be printed and stored in the file with the initial calibration to document evaluation. The analyst should select the regression order, which introduces the least calibration error into the quantitation and minimizes the y-intercept value (constant term).

Linear and Quadratic Regressions each have several options available in the software. The analyst must chose which order will be used. Options available are equal weighting, inverse of conc., and inverse square of conc.. The analyst should choose the curve order and weighting which gives the best coefficient of the determination (COD) and a y-intercept nearest to the origin, given the calibration blank is clean.

The percent relative standard deviation ***must*** be less than 15% for each compound. However, the % RSD for each individual

calibration check compound (CCC) ***must*** be less than 30%. Late-eluting compounds usually have much better agreement. The CCCs are:

1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl chloride

If the % RSD greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and / or column reactive sites is required before attempting another calibration.

7.1.4.2 A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average relative response factor. These compounds are:

Chloromethane	0.1
1,1-Dichloroethane	0.1
Bromoform	0.1
1,1,2,2-Tetrachloroethane	0.3
Chlorobenzene	0.3

These compounds typically have RFs of 0.4 - 0.6 and are used to check compound stability and to check degradation caused by contaminated lines or active sites in the system. See Table 2 for summary of the acceptance limits.

The analyst may drop the lowest or highest point for an analyte, possibly requiring either a change in reporting limits or narrowing the calibration range. An entire level may be deleted if there is cause to believe there was a poor injection, etc. The section head should examine the calibration to ensure the proper procedures were followed.

Table 3
Criteria for Initial and Continuing Calibration for 8260B

Volatile Compound		Initial and Continuing Calibration Minimum RRF	Initial Calibration Maximum % RSD	Continuing Calibration Maximum % Drift
Chloromethane	(SPCC)	(0.100)		
Vinyl chloride	(CCC)		(30%)	(20%)
1,1-Dichlororethane	(SPCC)	(0.100)		
1-1-Dichloroethene	(CCC)		(30%)	(20%)
Chloroform	(CCC)		(30%)	(20%)
Bromoform	(SPCC)	(0.100)		
1,1,2,2-Tetrachloroethane	(SPCC)	(0.300)		
Toluene	(CCC)		(30%)	(20%)
Chlorobenzene	(SPCC)	(0.300)		
Ethylbenzene	(CCC)		(30%)	(20%)
1,2 Dichloropropane	(CCC)		(30%)	(20%)

9.5 GC/MS Daily Calibration Procedure:

9.5.1 Daily Calibration Check:

9.5.1.1 The 8260 standard (continuing calibration at 25ppb but varied periodically) must pass 8260B criteria to continue. The average response factor or calibration curve of the initial calibration is verified daily using a calibration standard and must meet the criteria of CCC's <20% drift.

% Drift = c1 - c2/c1 x 100

where: c1 is the analyte concentration
c2 is the standard concentration

9.5.1.2 The five SPCC compounds are checked for a minimum average relative response factors. The acceptance criteria is listed in Table 2.

9.5.1.3 The internal standards must be monitored for retention time and area of response. The internal standard areas may not vary by more than - 50% or + 200% and their retention times by ±30 seconds from the comparable standard in the initial calibration.

9.5.1.4 If a standard does not pass it may be analyzed again, but if it fails the second time, the system should be checked for problems and corrected. Common causes of failure are: (1) purge flow too slow which will depress the RRFs of the poor purgers like bromoform and 1,1,2,2-tetrachloroethane, (2) purge flow too fast which will depress the RRFs of the gas analytes like chloromethane, (3) contamination in the autosampler/purge&trap system trap, valves, or lines which can degrade 1,1-dichloroethane and 1,1,2,2-tetrachloroethane.

9.5.15 New initial calibrations are always analyzed after major system changes such as replacing filaments, cleaning the source, significant re-tuning of the mass spectrometer, significant changes in purge & trap conditions, etc.

Laboratory Control Sample : A LCS is prepared using 100µL in 50ml DI of a 10ng/µL secondary source standard. For soil LCS, 2 mL Methanol, 100µL of 10 ng/µL second Source standard mix in 50 ml DI is used.

If any of the five (short list) compounds of the LCS do not meet acceptance criteria generated in-house every 12 months, the LCS may be re-analyzed. If the acceptance criteria are still not met the system is checked for problems and corrected before samples are analyzed. The limits are listed in Section 9.5

9.5.3 Blank analysis: A 5 mL aliquot of volatile free laboratory water is analyzed in the same manner as standards and samples to demonstrate that the system is interference free. When this has been demonstrated sample analysis may begin. A hardcopy of the blank chromatogram and quant output page is filed with the daily calibration data. The blank should not contain any analyte above one half the reporting limit with the possible exception of common laboratory contaminants such as Acetone and Methylene Chloride. The common laboratory contaminants must be less than the reporting limit. If there are any analytes over these limits and the samples are positive for these analytes, the samples must be re-analyzed when possible. If re-analysis is not possible, all results must be appropriately qualified on the client's report.

10.0 SAMPLE PROCEDURE

10.1 Preparation of Samples

Once the calibration procedure has been successfully completed the analysis of actual samples may begin. It is the responsibility of the GC/MS operator to follow these procedures. To determine which samples need to be analyzed on a given day, a daily work list is printed and used by the analyst to know when the analysis needs to be completed to satisfy the preservation / holding time requirements and the client's requests.

10.1.1 Preserved aqueous samples must be analyzed within 14 days from date of sampling. The pH must be <2.

10.1.2 In general, water samples are analyzed at 5 mL unless there is a known history of contamination in the sample or some matrix problem which requires a dilution to be analyzed. For a dilution of 1:10, 5mls of sample is removed with a gastight syringe and added to a 50ml volumetric flask containing distilled water. VOA Reagent water is added to the 50mL mark, capped, the volumetric is inverted three times, and poured gently into a VOA vial for analysis.The Dynatrap and the Archon Autosamplers are capable of performing a 1:10 dilution directly from a VOA vial placed in the tray for sample analysis.

10.1.2.1 All water samples, standards and blanks are spiked with internal standards and surrogate standards at 25µg/l prior to analysis by the instrument.

10.1.2.2 Allow samples to come to room temperature.

10.1.2.3 Aqueous samples are checked the day after analysis with low range pH paper to ensure it was preserved to a pH <2 at the time of collection. If pH is >2 , the duplicate vials are checked to determine if one has a pH<2. If a vial is found , the sample is re-analyzed. Otherwise,it is noted in the case narrative.

Soil samples are extracted by weighing out 20 grams of sample into a 40-mL vial and adding 20 mL of methanol and spiked with 40ul of surrogate mix. The weights and

the procedure used are recorded in the Soil Prep Log. Methanol blanks and a LCS are prepared each day soils are analyzed. 20 mls of methanol is added to a VOA vial and spiked with 40ul of surrogate mix. The LCS also has 100ul of the QC mix containing 60 compounds added upon dilution into a 50ml volumetric. For every twenty soil samples a spike and spike duplicate are prepared by spiking 100ul of a 10ng/ul mix in to a 50ml volumetric containing 2mls of a methanol extraction. EPA 5035 Methanol Field Preserved ,VPH, and New Jersey soils are extracted on-site using the VOA vials containing methanol that were prepared in the laboratory.

Soil samples must be extracted and analyzed within 14 days from the date of collection. EnCore samplers soil contents must be preserved in methanol or sodium bisulfate solution within 48 hours of sampling and analyzed within 14 days from collection.

10.2 Analysis of Samples

10.2.1 Every analytical batch of samples requires the following:

- BFB TUNE
- 8260 STANDARD (at 25ppb usually but concentration varied)
- LABORATORY CONTROL SAMPLE (LCS) – 20 µg/L
- PROCEDURAL(METHOD) BLANK
- SAMPLES
- MS/MSD- For every 20 client samples a spike and spike duplicate is required. They are spiked by AMRO with the LCS spike containing 60 compounds which include the five required by 8260. 100µl of a 10ng/µl mix is added to a 50ml volumetric containing 10mls of a water sample. Samples must be selected for spiking at random and rotated among clients and sites from batch to batch. In some cases, the client may specify which sample is to used for MS/MSD; if not , the laboratory shall pick a representative sample based on the following:

  A. MS/MSD shall not be performed on Trip Blank, Rinsate Blank or Field Blank.
  B. Adequate sample weight/volume.
  C. Client requested QC deliverables.

10.2.2 Samples and standards are introduced to the GC/MS System using 40mL VOA vials which are put into the autosampler tray. The autosampler syringe delivers 5mL to the purging chamber along with the internal standards and surrogates (the autosampler is equipped with a syringe or vial, which the operator fills with the internal standard and surrogate mix for waters). Also, a 40mL VOA vial containing Bromofluorobenzene (BFB) at a concentration of 50ng/5mL is placed on the tray for tuning (no SS is added).

10.2.3 Check the reservoir for water.

10.2.4 Check the IS and SS vials.

10.2.5 Type in the sequence of samples into the computer.

10.2.6 Recheck the vials in the autosampler to make sure they match the typed sequence.

10.2.7 Check the Helium.

10.2.8 Helium purges through the chamber and the volatile analytes are absorbed on the trap, a tube containing an OV-1/Tenax/Silica Gel/Charcoal mixture. After purging is complete, the trap is heated and backflushed with helium to desorb the compounds. The analytes are carried along a heated transfer line to the GC inlet, where the glass liner meets the narrow bore capillary column. At this point the analytes are heated, mixed and split. The column is temperature programmed to separate the analytes and is interfaced by a Mass Spectrometer for detection.

10.2.9 The raw data will print from the instrument as each sample is running.

10.3 Evaluation of Results

10.3.1 Identification of Compounds (Qualification)

Carefully evaluate the EICP and sample to reference spectrum match for each hit above or near the reporting limit that is detected by the data system. The qualitative identification of compounds is based on retention time and on the comparison of the sample mass spectrum, after background subtraction, with characteristic ions in a reference mass spectrum. The

characteristic ions are the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than 3 such ions occur in the reference spectrum. Compounds are identified as being present if:

- The intensities of the characteristic ions of a compound maximize in the same scan within one scan of each other.

- The relative retention time of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

- The relative intensities of the characteristic ions agree within 20% of the relative intensities of those ions in the reference spectrum.

10.3.1.1 All 624 target isomers are reported individually, with the exception of m- and p-xylene, which co-elute and are reported as an isomer sum. All other target isomers should meet the following resolution requirement: Sufficient GC resolution is achieved if the height of the valley between the two isomer peaks is less than 25% of the sum of the two peak heights.

10.3.1.2 Print a hardcopy of the graphics display In QEDIT for all confirmed positive results in client samples. Make certain the reference and sample spectra are included, as well as the properly displayed EICP. Do Not **Background correct** the sample spectrum.

10.3.1.3 Clients sometimes ask for identification of the 10 to 20 largest non-target peaks in sample chromatograms, referred to as Tentatively Identified Compounds (TICs). The Hewlett Packard Enviroquant Library Search Compounds (LSC) program will automatically print out the spectral PBM search results for the largest peaks (operator chooses the number) along with possible matches for

their spectra. The operator decides whether there is a good match of the sample and reference spectra or the spectrum remains classified as "unknown". Use the following guidelines when making tentative identifications:

- Relative intensities of the major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or the presence of coeluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

10.4 Quantitation of Compounds

The identified compound will be quantitated based on its response compared to that of its internal standard.

10.4.1 When the mass spectrometer is linear, the concentration of each analyte in the sample is, for water samples:

$$\text{Concentration } \mu g/L = \frac{(Ax)(Is)(5mL)}{(Ais)(RF)(Vo)}$$

Ax = area of characteristic ion for compound being measured
Is = amount of internal standard injected (ng)
Ais = area of characteristic ion for internal standard
RF = mean relative response factor for compound being measured

Vo = volume of water purged in mL.

10.4.2 The integration of compounds for standards and samples should be performed to be in the same manner as the initial calibration integration. Cases where the initial calibration is in question should be investigated to ensure it is not related to poor maintenance, damaged or defective column, or other issues, which should be solved before further analysis.

10.4.3 The following must be checked for each compound present in standards and samples to ensure proper integration has been performed.

- The peak shape of the calibration compound must be maintained for standards and samples. This should take into account any shouldering, peak tailing, and peak co-elution. Carefully evaluate the EICP of each gas analyte , all ketone targets (esp. acetone and 2-butanone), methylene chloride, all esters, and tetrahydrofuran for proper integration in all standards and samples because these targets often exhibit broad peaks and poor signal to noise ratios. Carefully examine the following target hits due to posible misidentification by the data system: chloroethane, 1,2,3-trichloropropane, 4-methyl-2-pentanone , n-propyl benzene, 2- chlorotoluene, and the dichlorobenzene isomers.

- The EICP retention time windows for each compound of the calibration must be applied to standards and samples. If there is a retention time shift confirmed by comparison of the Internal Standards and Surrogates then carefully examine each EICP for potential target shifts. Watch especially in the narrow retention time windows where a shift might cause all or part of a peak to leave the window and be missed or mis-integrated by the data system. If false negatives due to retention time

shifting appear likely then the sample must be reanalyzed.

- The baseline integration techniques for each compound of the calibration must be maintained for the standards and the samples. This should take into account elevated baselines, column compensation corrections and negative peaks in samples.

- Make sure that positive identification of compounds has been established thru EICP's and all method requirements have been met.

- Ensure any positive results are within the lower and upper levels of the calibration curve and above the reporting limits for each compound. All positive results above the calibration curve must be reanalyzed in dilution.

10.4.4 If there are any cases where the integration or spectral identification of a compound is questionable after ensuring the above steps have been followed then consult another qualified analyst. "Before" and "After" chromatograms and spectra should be printed in these cases, dated and initialed by the analyst and the qualified consultant.

10.4.5 Analytes with initial calibration RRFs >15%RSD are fitted to a linear regression or quadratic regression in the initial calibration. The software will automatically quantitiate the analyte by the parameters set for the initial calibration, average response, linear regression or quadratic regression.

10.4.6 Clients may ask for estimated concentrations of non-calibrated compounds. The Hewlett Packard LSC software will do this automatically, requiring only a dilution factor.

10.4.7 Once all the data has been evaluated it is submitted for data review. The following must be submitted for each project:

10.4.7.1 The raw data from the instrument that was printed while the sample was running. This consists of the quantitiation report and the chromatograms.

10.4.7.2 The data after it has been reviewed by the analyst. This consists of the quantitiation report that was reviewed.

10.4.7.3 A copy of the injection log(s) associated with the samples for the project.

10.4.7.4 Copies of the preparation sheets associated with the samples.

10.4.7.5 A copy of the applicable blanks if the project is a Level 2 package or higher. See the Quality Systems Manual for Package Levels.

10.4.7.6 If the project is a Level 4 or 5, copies of the following items must be provided to data review: Initial Calibration summary and raw data along with the information described in sections 10.4.7.1 to 10.4.7.5 are required.

10.4.7.7 The GC/MS Checklist is completed by the analyst that provides an overview of the issues associated with the data. Any items that do not meet acceptable criteria must be qualified by the analyst in the form of a documented investigation of the issue(s) written on the narrative form.

11.0 INSTRUMENT PREVENTATIVE MAINTENANCE AND REPAIR

Instrument maintenance and repair records are maintained to document satisfactory instrument performance. The operator is generally responsible to see that records are well kept. Records of major maintenance and repair are kept in the instrument maintenance log per instrument. Routine maintenance procedures such as changing the GC septum need only be recorded in the instrument analysis log.

11.1 Daily maintenance procedures:

The following items should be checked on every day that an instrument is used for analysis.

11.1.1 Trap and column performance. This is monitored by checking the response factor of key compounds, which indicate trap and column degradation and observing column bleed. Change trap or column if necessary.

11.1.2 Check that gases have adequate supply to last until the following day. Change tanks if necessary.

11.1.3 Check data file space and quant space.

11.2 Biweekly maintenance procedures:

The following items should be done every two weeks:

11.2.1 Check split flow on GC.

11.2.2 Check purge gas flow on the purge&trap. Adjust if necessary.

11.2.3 Check Teflon ferrules on purge&trap for wear. Replace if necessary.

11.2.4 Check Teflon purge lines on purge&trap for wear. Replace if necessary.

11.3 Three month maintenance procedure:

11.3.1 Every 3 months the o-rings, Teflon block should be replaced and intake filters should be vacuumed.

11.4 Six month maintenance procedure:

11.4.1 Every 6 months the vacuum pump oil should be changed.

11.5 Maintenance "As needed":

The following service should be performed when system performance indicates.

11.5.1 Clean the analyzer source. This will become necessary if a high background becomes apparent which is not attributable to column degradation or the system cannot meet BFB criteria.

11.5.2 Replace the electron multiplier when the maximum gain no longer provides the required sensitivity.

11.5.3 Replace the ion source filament as needed.

12.0 CALCULATIONS

12.1 Refer to Section 10.4

13.0 QUALITY CONTROL

A formal quality control program is in operation at the present time at AMRO. The Laboratory Control limits for surrogate, matrix spikes and laboratory control sample spike are updated on an annual basis.

13.1 Standards

13.1.1 The spiking solutions are obtained commercially. New lots of spiking solution are compared to the ones currently in use before being used. If they differ by more than 10%, then replace spike. If still out, new calibration curves will probably need to be prepared with the new solutions.

13.2 Internal standard

13.2.1 All samples, standards, and blanks are spiked with internal standards at 25 µg/l in water and soil extractions prior to analysis. Internal standard areas are monitored.

13.2.2 If examination of the total ion chromatogram shows no evidence of matrix interference or elevated baseline, the samples should be re-analyzed to determine if there is some other matrix effect behavior or that the added internal standard solution is no longer acceptable for use. If re-analysis exhibits

the same behavior then the analyst will report the data and generate a Non-Conformance report with some assessment of data impact.

13.2.3 If examination of the total ion chromatogram shows evidence of matrix interference or elevated baseline, the analyst should evaluate whether a dilution is warranted due to peak distortion. If there are no chromatographic anomalies, the data is reported as is since the internal standard is designed to allow for some matrix effects or inlet discrimination.

13.3 Surrogates

13.3.1 All samples, standards, and blanks are spiked with surrogate standards at 25 µg/l in water and low soil analysis, and at 100ug/l in methanol preserved soils prior to analysis. Surrogate recoveries are monitored. Surrogate recoveries for samples are input into spreadsheets to calculate mean and standard deviation and to establish laboratory guidelines for recovery limits. In house limits are generated on an annual basis. If the percent recovery for any surrogate compound is found to be out of acceptable range, the data must be evaluated. If the surrogate recovery is outside of the upper acceptance limit and there is an assignable cause, the data can be reported with a note of qualification. If the surrogate recovery is outside of the range and there is no assignable cause, the sample must be re-analyzed. If it is not possible to re-analyzed the samples due to hold time constraints, the data must be qualified.

VOA WATER SURROGATES

ANALYTE	SAMPLE/BLK/LCS AS OF 01/2001
1,2-Dichloroethane-d4	75-124%
Toluene-d8	86-111%
Bromofluorobenzene	76-113%
Dibromofluoromethane	85-118%

VOA MEDIUM LEVEL SOIL SURROGATES

ANALYTE	SAMPLE/BLK/LCS AS OF 01/2001
1,2-Dichloroethane-d4	55-127%
Toluene-d8	67-124%
Bromofluorobenzene	63-120%
Dibromofluoromethane	63-121%

VOA LOW LEVEL SOIL SURROGATES

ANALYTE	SAMPLE/BLK/LCS AS OF 01/2001
1,2-Dichloroethane-d4	72-136%
Toluene-d8	73-114%
Bromofluorobenzene	71-118%
Dibromofluoromethane	71-123%

13.4 Blanks

13.4.1 Blanks are analyzed daily. Soil extraction method blanks are analyzed with soils. Blanks are evaluated to ensure analyte levels are below reporting limits. If any compounds are seen in blanks greater than one half the reporting limit, the system is checked for contamination, and the blank is re-analyzed. If common laboratory contaminants Methylene Chloride and/or Acetone are present above the reporting limits and samples contain positive results for these analytes the samples must be reanalyzed or reported with B flag qualifiers. AMRO has observed Naphthalene presence in the blanks at levels below reporting limits due to carryover from the VPH Standard containing 100 ppb of Naphthalene. Analysis should not proceed if the initial blanks are greater than one half the reporting limit for any other analytes and the problem can be corrected by instrument adjustment or cleaning, e.g. analyzing additional blanks

13.4.2 Trip blanks are analyzed along with the samples they arrived at the lab with. Their purpose is to assess the possibility of cross-contamination of the samples while in transport. If provided, they are analyzed with the samples they are used to assess.

13.4.3 Field blanks are also analyzed when they are provided by the client.

13.5 Laboratory Control Samples

13.5.1 Laboratory Control Samples (LCS) are prepared with samples and analyzed with the sample matrix they correspond to. The LCS for water contains all target analytes. *If LCS does not produce acceptable recoveries based on 8260 limits then they are re-analyzed. If the LCS is still unacceptable, the LCS solution is checked, as well as the calibration. If the LCS is not acceptable the LCS is re-analyzed before any samples are run.*

13.5.2 Listed below the current Laboratory Control Sample control limits as of 01/2001:

VOA LCS LIMITS

Analyte	WaterLCS Limits	Medium Level Soil LCS	Low Level Soil LCS*
1,1-Dichlorethene	71-134%	59-139%	70-130%
Benzene	80-122%	71-123%	70-130%
Trichloroethene	83-117%	70-121%	70-130%
Toluene	84-118%	74-120%	70-130%
Chlorobenzene	85-119%	76-124%	70-130%

*8260B default limits are in place until enough data points have been accumulated.

13.6 Matrix Spikes

13.6.1 For aqueous samples, an MS and an MSD must be analyzed with every 20 sample analytical batch.

13.6.2 Listed below the current Matrix Spike control limits as of 01/2001:

Analyte	WaterMS Limits	Medium Level Soil MS	Low Level Soil MS*
1,1-Dichlorethene	69-136%	56-143%	70-130%
Benzene	76-127%	71-125%	70-130%
Trichloroethene	80-121%	71-125%	70-130%
Toluene	83-122%	73-126%	70-130%
Chlorobenzene	83-122%	76-126%	70-130%

*8260B default limits are in place until enough data points have been accumulated

13.6.3 If the results of both matrix spike samples do not meet acceptance criteria then matrix interference is suspected. The Laboratory Control Sample (LCS) is reported to prove that the system is 'in-control' and the spike results are suspected to be due to matrix interference, providing the LCS was acceptable.

13.7 Duplicates

13.7.1 A duplicate is analyzed for every 20 samples in the form of a Matrix Spike/Matrix Spike Duplicate. The results are evaluated to ensure acceptable reproducibility for the analysis. The Relative Percent Difference (RPD) between the concentrations of the analysis are calculated as follows:

$$\%RPD = \frac{(MS\ conc. - MSD\ conc)}{(MS\ conc. + MSD\ conc.)/2)} * 100$$

13.7.3 The %RPD must be ≤25%.

13.7.4 If the %RPD is not acceptable then an assignable cause such as sample non-homogeneity or carry over from a high sample, etc is explored. If a reasonable cause is found the batch is accepted, if not the MS and MSD are reanalyzed.

13.8 Corrective Action

13.8.1 Problems that are identified at the bench level and are corrected by the analysts are noted on the GC/MS Data Review Checklist, Attachment 2. If any non-conformance is determined by lab manager review, a QC review or Corrective Action is to be included with the applicable report. Sections are informed of non-conformance issues in an effort to prevent reoccurrence. Any issues that are made evident by a client, resulting in corrective actions being completed which identify the issue, cause and correction. This information is provided to the client.

14.0 DATA REVIEW AND STORAGE

AMRO's goal for completeness is 100%. The following data calculating, reviewing and reporting procedures are followed to obtain that goal.

14.1 Data Validation - performed by the analyst:

When an analysis of a sample is complete, the analysis for that sample should be checked and the data calculated as soon as possible to identify any problems while still within the holding time for the analysis. The following steps should be taken to ensure that a good analysis has been obtained.

14.1.1 Check that all calibration analyses associated with the sample meet criteria to ensure acceptance criteria is met.

14.1.2 Check the internal standard areas. They should be -50 to +200% of the I.S. areas in the Initial Calibration standard.

14.1.3 Compare the surrogate recoveries to the AMRO limits. The default VOA surrogate recovery limits are as follows and are used until in house limits are generated.

14.1.4 Check the LCS to be sure the results are inside the limits, as well as the matrix spike and matrix spike duplicate results.

14.1.5 Check the analyzed times to be sure the tuning requirements are met.

14.1.6 Check that no compounds exceed the calibration range. If there are, these samples must be reanalyzed at a dilution.

14.1.7 Check the chromatography (good peak shape, baseline not noisy, good sensitivity).

14.1.8 Check the analysis for carryover or contamination. If any carryover is evident, these samples must be reanalyzed.

14.1.9 Check that the amount of sample analyzed is correctly recorded in the chromatogram header.

14.1.10 Check spectrum, area, and retention time of any positive hits on the quant output page.

14.1.11 Perform the final calculations on any positively identified compound in µg/L, taking into account dilution factors, etc.

Calculate the multiplier which equals grams of sample purged and write it on the quant output page. The soil multiplier is calculated by the following calculation:

$$\text{grams sample purged} = \frac{\text{sample wt. grams}}{\text{mL Methanol extracted}} \times \frac{\%\ \text{solids}}{100} \times \text{mL Methanol purged}$$

soil multiplier = 5mls purge/ gms sample purged

14.1.12 Check the chromatogram for very large peaks not picked up by quant. If any are present, check the spectrum to be sure it is not a target compound that is over the calibration range or

outside the normal retention time window. If not a target compound, make a note on the chromatogram that the peak is an unknown and use the library to identify if possible.

14.1.13 Check to see if there are any other analyses of the sample. If so, check to see if the data agrees.

Any problems discovered during this preliminary data check will necessitate re-analysis unless the lab manager authorizes use of the data in writing with an explanation of why the data is being used.

All calculations should be written in black ballpoint pen ink. All cross-outs should be a single line and should be initialed. The person performing these data calculations and checks should sign and date the bottom of the quant page.

14.2 Data Review - performed by the department supervisor or designate.

When all samples for a given project have been analyzed and the results have been calculated, the project goes through the following data review procedure:

14.2.1 The reviewer reads over all associated paperwork to become familiar with the requirements of the project.

14.2.2 The project is checked for completeness.

14.2.3 Data sheets are checked for accuracy.

14.2.4 The data calculations are spot-checked. If any problems are encountered then the whole package should be checked.

14.2.5 The QC data sheets are checked.

Any problems encountered by the reviewer are brought to the attention of the lab manager.

14.3 Data Reporting

Many report options are available to clients of AMRO. It is AMRO policy to discuss with all clients their reporting requirements soon after receipt of the samples. The cover letter for the data reports will address any quality control problems, either with the condition of the samples upon receipt or with the analyses, or contain a statement that no quality control problems were encountered. The etter will also contain a statement that it is an integral part of the data report.

14.4 Data Archival

14.4.1 GC/MS Data Files.

All raw GC/MS data files are archived through the Network and are backed up on a tape drive through the server.

14.4.2 Data Reports.

Final data and QC reports are input into Excel and spreadsheet files. Template files exist on the Network for final data reports, daily QC check reports, sample spike reports, initial precision and accuracy data, wastewater method accuracy data, surrogate recovery data, and MDL data. When data is input template files are renamed as follows:

data reports XXX#####

Where X 's are the first three characters of the AMRO client code and #'s are the AMRO project and sample number.

15.0 REFERENCES

15.1 40 CFR Part 136 Appendix B, 1984.

15.2 USEPA Office of Solid and Hazardous Waste - SW-846 Method Chapter 1, Rev. 1 7/92.

15.3 USEPA Office of Solid and Hazardous Waste - SW-846 Method 8000B, Rev. 2 12/96.

15.4 USEPA Office of Solid and Hazardous Waste - SW-846 Method 8260B, Rev. 2 12/96

15.5 New Jersey Department of Environmental Protection "Methodology for the Field Extraction/Preservation of Soil Samples with Methanol for Volatile Organic Compounds", 2/97.

15.6 USACE Shell for Analytical Chemistry Requirements, EM200-1-3, 02/01/2001.

Attachment 1

AMRO Environmental
Laboratories Corporation

111 Herrick Street
Merrimack, NH 03054
(603) 424-2022

QUALIFICATION CARD FOR SW-846 METHOD 8260B

Trainee: _____ Signature: _____

Trainer: _____ Signature: _____

I. Knowledge Factors:

SOP Title: _____ Revision Number/Date: _____

1. Did the Trainee read and understand the above SOP?	Yes ☐	No ☐	NA ☐
2. Was the Trainee instructed on how to properly fill out the documentation?	Yes ☐	No ☐	NA ☐
3. Has the Trainee been instructed on the proper procedures for addressing potential problems?	Yes ☐	No ☐	NA ☐

II. Practical Factors:

1. Has the Trainee completed a Precision and Accuracy Study?	Yes ☐	No ☐	NA ☐
2. Has the Trainee completed an acceptable Performance Evaluation sample?	Yes ☐	No ☐	NA ☐
3. Did the Trainee completed an acceptable Laboratory Control Sample (LCS)?	Yes ☐	No ☐	NA ☐
4. Has the Trainee performed manual integration as indicated in the SOP?	Yes ☐	No ☐	NA ☐

Completion Date: _____ Trainer's Signature: _____

I _____ have read, understood and follow the above method/SOP, which is in use at AMRO Laboratories for the analysis of samples under the National Environmental Laboratory Accreditation Program, have met the Demonstration of Capability.

Section Manager/ Supervisor: _____ Date: _____

QA Manager: _____ Date: _____

qc/qcmemos/forms/8260Bqualcard Rev. 0 02/01

Attachment 2

AMRO Environmental
Laboratories Corporation

111 Herrick Street
Merrimack, NH 03054
(603) 424-2022

GC AND GC/MS DATA REVIEW CHECKLIST

LAB ORDER: _____ **CLIENT:** _____

Method:	**Sample(s) No.:**
Analysis:	**Matrix:**

A.	**GENERAL**			
1.	Copy of Prep/Extraction Log?	Y	N	NA
2.	Copy of Instrument Run Log or Tune List?	Y	N	NA
3.	Copy of dry weight log present?	Y	N	NA
4.	Are all sample checked for preservation after VOA analysis?	Y	N	NA
5.	All samples met extraction and/or analysis holding time criteria?	Y	N	NA
6.	Did the Tune pass and DFTPP or BFB injected every 12 hours?	Y	N	NA
7.	Are the surrogate recoveries for each sample within the QC limits?	Y	N	NA
8.	Method Blank- contaminant free?	Y	N	NA
9.	Initial Calibration meets method criteria for all compounds reported?	Y	N	NA
10.	Continuing Calibration meets method criteria for all compounds reported?	Y	N	NA
11.	Are all reported results within calibration range?	Y	N	NA
12.	LCS % Recovery criteria met for all compounds?	Y	N	NA
13.	MS/MSD %R's and %RPD's are met for all compounds?	Y	N	NA
14.	%RPD criteria met between sample and duplicate?	Y	N	NA
15.	Samples checked for carry over from sample to sample due to target or nontarget overload?	Y	N	NA
16.	Are all data exported to LIMS, calculated and verified?	Y	N	NA

COMMENTS

Analyst (s) _____ DATE: _____

REVIEWER: _____ DATE OF REVIEW: _____

qc/qcmemos/Forms/gcmschecklist Rev. 1 04/00

Attachment 3

This Data Sheet Contains Important Information About The Product.

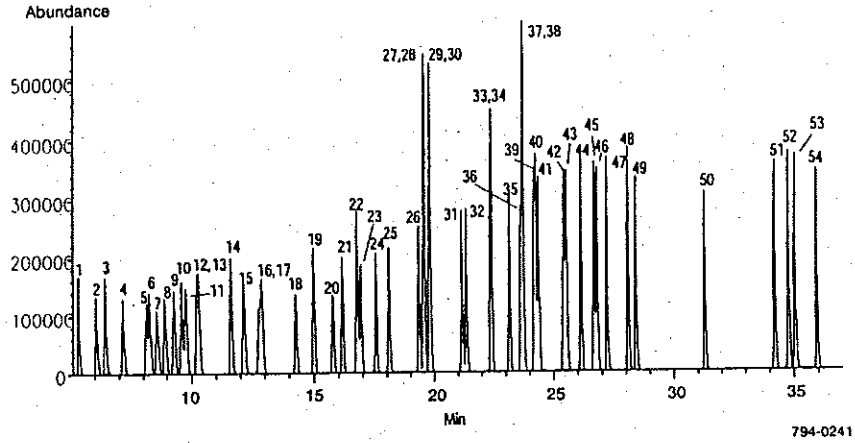
502/524 Volatile Organics Calibration Mix

Catalog No. 502111

This mixture contains 2000µg/mL of each of the following components in methanol:

1. 1,1-Dichloroethylene
2. Methylene chloride
3. trans-1,2-Dichloroethylene
4. 1,1-Dichloroethane
5. 2,2-Dichloropropane
6. cis-1,2-Dichloroethylene
7. Chloroform
8. Bromochloromethane
9. 1,1,1-Trichloroethane
10. 1,1-Dichloropropene
11. Carbon tetrachloride
12. 1,2-Dichloroethane
13. Benzene
14. Trichloroethylene
15. 1,2-Dichloropropane
16. Bromodichloromethane
17. Dibromomethane
18. cis-1,3-Dichloropropene
19. Toluene
20. trans-1,3-Dichloropropene
21. 1,1,2-Trichloroethane
22. Tetrachloroethylene
23. 1,3-Dichloropropane
24. Dibromochloromethane
25. 1,2-Dibromoethane
26. Chlorobenzene
27. Ethylbenzene
28. 1,1,1,2-Tetrachloroethane
29. m-Xylene
30. p-Xylene
31. o-Xylene
32. Styrene
33. Bromoform
34. Isopropylbenzene
35. 1,1,2,2-Tetrachloroethane
36. 1,2,3-Trichloropropane
37. Bromobenzene
38. n-Propylbenzene
39. 2-Chlorotoluene
40. 1,3,5-Trimethylbenzene
41. 4-Chlorotoluene
42. tert-Butylbenzene
43. 1,2,4-Trimethylbenzene
44. sec-Butylbenzene
45. p-Isopropyltoluene
46. 1,3-Dichlorobenzene
47. 1,4-Dichlorobenzene
48. n-Butylbenzene
49. 1,2-Dichlorobenzene
50. 1,2-Dibromo-3-chloropropane
51. 1,2,4-Trichlorobenzene
52. Hexachlorobutadiene
53. Naphthalene
54. 1,2,3-Trichlorobenzene

TIC



Column: VOCOL™, 105m x 0.53mm ID, 1.0µm film
Oven: 35°C (4 min) to 200°C at 4°C/min
Carrier: helium, 15mL/min
Det.: MS (m/z = 35-260, 0.4 sec/scan)

T797016

SUPELCO
Bellefonte, PA

Attachment 4

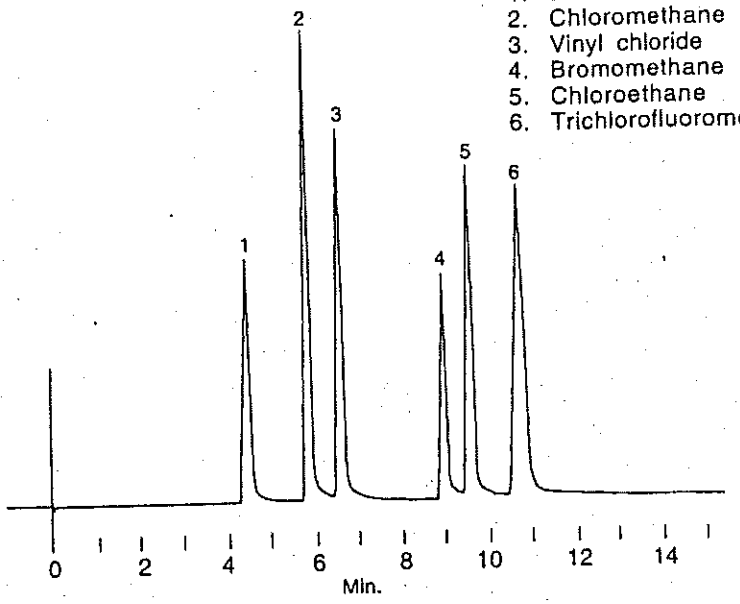
SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

VOC Mix 6

Catalog Numbers 48799-U/4S8799

This mixture contains 2000µg/mL of each of the following components in methanol:

1. Dichlorodifluoromethane
2. Chloromethane
3. Vinyl chloride
4. Bromomethane
5. Chloroethane
6. Trichlorofluoromethane



713-1268

Column: **VOCOL™, 105m x 0.53mm ID, 3.0µm film**
Cat. No.: **25358**
Col. Temp.: -10°C (3 min) to 60°C at 4°C/min
Carrier: helium, 10mL/min
Det.: Hall®, 250°C
Inj.: 1µL, 200°C

SUPELCO
Bellefonte, PA

DS97953D

Attachment 5A

RESTEK CORPORATION

CERTIFICATE OF ANALYSIS

FOR LABORATORY USE ONLY—READ MSDS PRIOR TO USE.

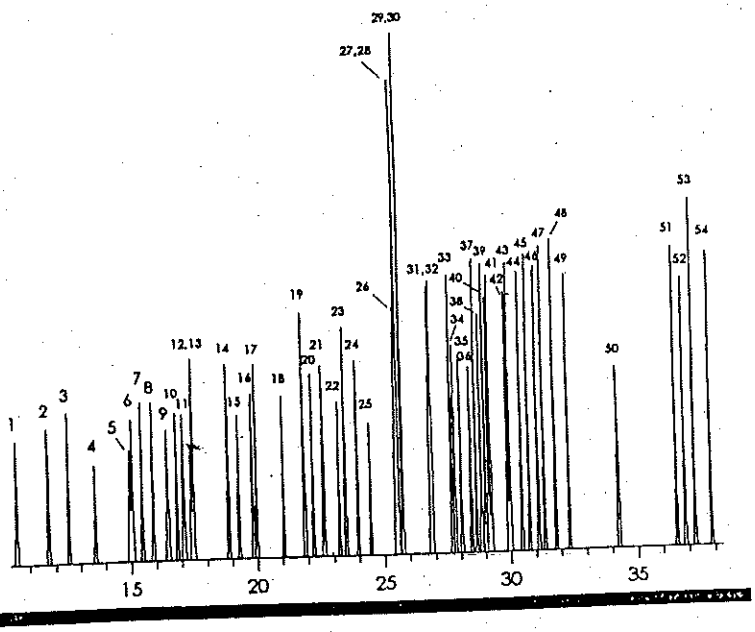
Cat. No.: 30431 Lot No.: A016490

Description: 502.2 CAL 2000 MegaMix™

PAGE 3

Elution Order	Compound
1	1,1-dichloroethene
2	methylene chloride
3	trans-1,2-dichloroethene
4	1,1-dichloroethane
5	2,2-dichloropropane
6	cis-1,2-dichloroethene
7	chloroform
8	bromochloromethane
9	1,1,1-trichloroethane
10	1,1-dichloropropene
11	carbon tetrachloride
12	1,2-dichloroethane
13	benzene
14	trichloroethene
15	1,2-dichloropropane
16	bromodichloromethane
17	dibromomethane
18	cis-1,3-dichloropropene
19	toluene
20	trans-1,3-dichloropropene
21	1,1,2-trichloroethane
22	1,3-dichloropropane
23	tetrachloroethene
24	dibromochloromethane
25	1,2-dibromoethane
26	chlorobenzene

Column: 105m .32mm 1.8µm Rtx®-502.2 (cat.# 10921)
Carrier gas: helium @ 2.2 ml/min.
Temp. program: 40°C (hold 6 min.) to 240°C @ 6°C/min (hold 5 min.)
Inj. temp.: 200°C
Det. temp.: 250°C
Detector type: MSD



John Lidgett—QA Analyst

ISO 9001 REGISTERED

MANUFACTURED UNDER RESTEK'S ISO 9001 REGISTERED QUALITY SYSTEM: Certificate #97-HOU-AQ-8550 issued by DNV Certification, Inc.

Attachment 5B

RESTEK CORPORATION

CERTIFICATE OF ANALYSIS

FOR LABORATORY USE ONLY—READ MSDS PRIOR TO USE.

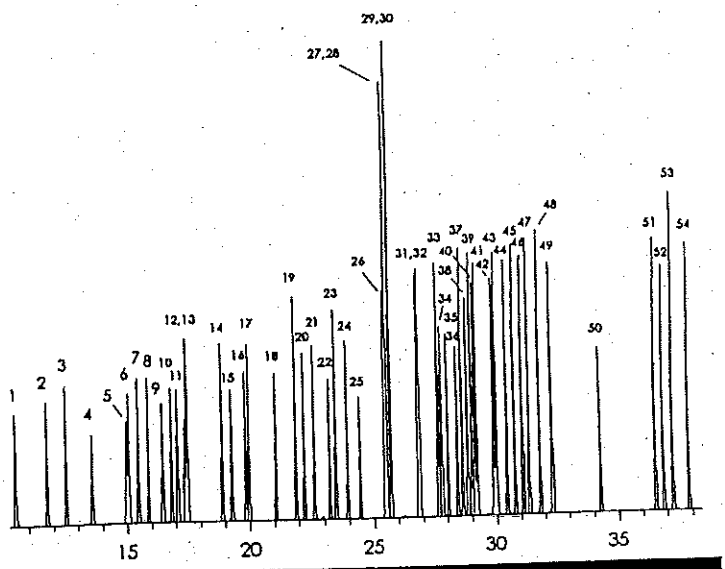
Cat. No.: 30431 Lot No.: A016490

Description: 502.2 CAL2000 MegaMix™

PAGE 4

Elution Order	Compound
27	1,1,1,2-tetrachloroethane
28	ethylbenzene
29	m-xylene
30	p-xylene
31	o-xylene
32	styrene
33	isopropylbenzene
34	bromoform
35	1,1,2,2-tetrachloroethane
36	1,2,3-trichloropropane
37	n-propylbenzene
38	bromobenzene
39	1,3,5-trimethylbenzene
40	2-chlorotoluene
41	4-chlorotoluene
42	tert-butylbenzene
43	1,2,4-trimethylbenzene
44	sec-butylbenzene
45	p-isopropyltoluene
46	1,3-dichlorobenzene
47	1,4-dichlorobenzene
48	n-butylbenzene
49	1,2-dichlorobenzene
50	1,2-dibromo-3-chloropropane
51	1,2,4-trichlorobenzene
52	hexachlorobutadiene
53	naphthalene
54	1,2,3-trichlorobenzene

Column: 105m .32mm 1.8µm Rtx®-502.2 (cat.#10921)
Carrier gas: helium @ 2.2 ml/min.
Temp. program: 40°C (hold 6 min.) to 240°C @ 6°C/min.(hold 5 min.)
Inj. temp.: 200°C
Det. temp.: 250°C
Detector type: MSD



John Lidgett

John Lidgett—QA Analyst

ISO 9001 REGISTERED

MANUFACTURED UNDER RESTEK'S ISO 9001 REGISTERED QUALITY SYSTEM: Certificate #97-HOU-AQ-8550 issued by DNV Certification, Inc.

Attachment 6

RESTEK

CERTIFICATE OF ANALYSIS

110 Benner Circle
Bellefonte, PA 16823-8812
Tel.: (800)356-1688
Fax: (814)353-1309

A03995

FOR LABORATORY USE ONLY—READ MSDS PRIOR TO USE.

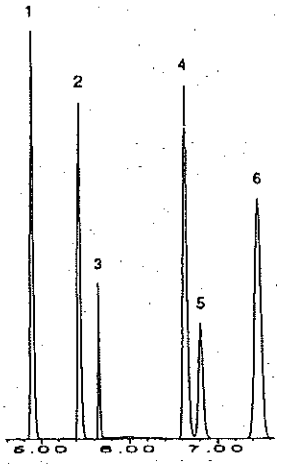
Cat. No.: 30042 Lot No.: A018640

Description: 502.2 Calibration Mix #1

Expiration Date[1]: September 2007

Elution Order	Compound[2]	CAS#	Percent Purity[3]	Concentration (weight/volume)[4]	Percent Uncertainty[5]
4	bromomethane	74-83-9	99%	1,995 µg/ml	± 1.3%
5	chloroethane	75-00-3	99%	1,996 µg/ml	± 1.4%
2	chloromethane	74-87-3	99%	2,006 µg/ml	± 1.4%
1	dichlorodifluoromethane	75-71-8	99%	1,999 µg/ml	± 1.3%
6	trichlorofluoromethane	75-69-4	99%	2,000 µg/ml	± 0.3%
3	vinyl chloride	75-01-4	99%	2,002 µg/ml	± 1.6%
Solvent:	purge and trap methanol	67-56-1	99%		

Column: 105m .32mm 1.8µm
Rtx®-502.2 (cat.#10921)
Carrier gas: helium @ 2.2 ml/min.
Temp. program: 50°C Isothermal
(hold 12 min.)
Inj. temp.: 240°C
Det. temp.: 240°C
Detector type: MSD



John Lidgett

John Lidgett—QA Analyst

[1]Expiration date of the unopened ampul stored at recommended temperature.

[2]Listed in alphabetical order.

[3]As determined by capillary GC/FID unless otherwise noted. Value rounded to the nearest LOWER whole percentage. In addition to GC/FID, chemical identity and purity are confirmed using 2 or more of the following: GC/MS, solid probe MS, GC/ECD, GC/FPD, GC/NPD, GC/TC, HPLC, DSC, FTIR, melting point, refractive index, and Karl Fisher.

[4]Based upon gravimetric preparation with balance calibration verified using NIST traceable weights (seven mass levels).

[5]Percent uncertainty based upon balance AND ASTM Class A volumetric glassware accuracy.

ISO 9001 REGISTERED RESTEK QUALITY SEPARATES US FROM THE REST

MANUFACTURED UNDER RESTEK'S ISO 9001 REGISTERED QUALITY SYSTEM: Certificate #97-HOU-AQ-8550 Issued by DNV Certification, Inc.

AMRO Environmental Laboratories Corporation

111 Herrick Street, Merrimack, NH 03054
TEL: (603) 424-2022 · FAX: (603) 429-8496

METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (VPH) BY GC/MS

Revision No.: 0

Revision Date: 04/03/2001

Prepared By: Suzanne Karam Date: 04/05/01

Approved By: Suzanne Karam Date: 04/05/01
VOA Supervisor

Approved By: Date: 04/06/01
Organic Manager

Approved By: Date: 04/06/01
Laboratory Director

Approved By: Date: 04/06/01
Quality Assurance Manager

TABLE OF CONTENT

1.0 SCOPE and APPLICATION

1.1 This method is designed to measure the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil. Volatile aliphatic hydrocarbons are collectively quantitated within two ranges: C_5 through C_8, and C_9 through C_{12}. Volatile aromatic hydrocarbons are collectively quantitated within the C_9 to C_{10} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C and 220°C.

1.2 This method is also able to measure the individual concentrations of the VPH Target Analytes benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and methyl-tert-butylether (MTBE) in water and soil. Use of this method to identify and quantitate these Target Analytes is optional.

1.3 Petroleum products suitable for evaluation by this method include gasoline, mineral spirits, and certain petroleum naphthas. This method, in and of itself, is not suitable for the evaluation of kerosene, jet fuel, heating oils, lubricating oils, and/or other petroleum products which contain a significant percentage of hydrocarbons heavier than C_{12}.

1.4 The Reporting Limit (RL) of this method for each of the collective aliphatic and aromatic fractional ranges is approximately 1-3 mg/kg in soil, and approximately 25-100 µg/L in water. The RL of this method for Target Analytes is compound-specific, and ranges from approximately 0.1 to 0.2 mg/kg in soil and 2 to 5 µg/L in water.

1.5 This method includes a series of data manipulation steps to determine the concentrations of aliphatic and aromatic ranges of interest. These steps may be taken by the laboratory or by the data user. Data generated using this method must be reported using the form/format provided.

1.6 This procedure details the steps taken by AMRO Environmental Laboratories Corporation to produce accurate and reliable results for Volatile Petroleum Hydrocarbon using GC/MS Method.

1.7 The following lists of compounds are analyzed by purge and trap GC/MS using a 5mL aliquot of an aqueous sample or 5mL of water containing 200µl of a methanol extract for soil samples:

TABLE 1

CAS. NO.	COMPOUND	WATER REPORTING LIMITS (µg/L)	SOILS REPORTING LIMITS (mg/Kg)
1634-04-4	Methyl tert-butyl ether	2	0.050
71-43-2	Benzene	2	0.050
108-88-3	Toluene	2	0.050
100-41-4	Ethylbenzene	2	0.050
108-38-3	m-Xylene	2	0.050
106-42-3	p-Xylene	2	0.050
95-47-6	o-Xylene	2	0.050
91-20-3	Naphthalene	5	0.125
	C5-C8 Aliphatic Range	100	2.5
	C9-C12 Aliphatic Range	25	0.63
	C9-C10 Aromatic Range	25	0.63

2.0 METHOD SUMMARY

2.1 Samples are introduced to the GC/MS System by directly placing the VOA vials into the autosampler tray. Standards are prepared in volumetrics and transferred to 40mL VOA vials. The autosampler syringe delivers 5mL to the purging chamber along with the internal standards and surrogates (the autosampler is equipped with a syringe or vial, which the operator fills with the internal standard and surrogate mix for waters and internal standard mix for soils). Also, a 40mL VOA vial containing Bromofluorobenzne (BFB) at a concentration of 50ng/5mL is placed on the tray for tuning.

2.2 Helium purges through the chamber and the volatile analytes are absorbed on the trap, a tube containing an OV-1/Tenax/Silica Gel/Charcoal mixture. After purging is complete, the trap is heated and backflushed with helium to desorb the compounds. The analytes are carried along a heated transfer line to the GC inlet, where the glass liner meets the narrow bore capillary column. At this point the analytes are heated, mixed and split. The column is temperature programmed to separate the analytes and is interfaced by a Mass Spectrometer for detection.

2.3 Identification of target analytes is accomplished by comparing their mass spectra with that of standards. Quantitation is done by comparing the response of a major ion relative to that of an internal standard using from 8 to 10 point calibration curve.

2.4 Quantitation of the aliphatic and aromatic ranges are achieved by comparing the areas of the MS detector responses to a 13 component VPH standard containing target analytes and alkanes. The C5-C8 Aliphatic Range and C9-C12 Aliphatic Range is integrated using m/z 43 and the C9-C10 Aromatic Range is integrated using m/z 91.

2.5 The GC/MS operators should be thoroughly trained and skilled in the use of purge and trap GC/MS before being authorized to analyze and report sample results independently. All analysts shall complete Qualification Card for VPH Method.

2.6 Method Modification: The compounds listed above include the VPH compounds. The laboratory has demonstrated that these analytes are achievable through initial demonstration of capability. This method is based on SW-846 Methods 8260B, 5035B, and 5030B.

3.0 DEFINITIONS

3.1 **Method Blank:** An aliquot of reagent water, which is carried through the entire analytical procedure with the samples, its purpose is to determine whether contamination is present during the analysis. For soil samples preserved with methanol, the method blank contains 200ul of methanol per 5mL purge as do the samples. A method blank is analyzed 1 for every analytical batch of samples.

3.2 **Laboratory Control Sample:** An aliquot of reagent water which known quantities of the method analyte are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine the degree to which the analytical result approaches the "true value" of the concentration of the analyte being determined. For soil samples preserved with methanol, the LCS also contains 200µl per 5mL of methanol from a VPH VOA vial. The percentage recovery is calculated in order to assess the efficiency of the analysis. One (1) LCS is analyzed for every analytical batch of samples.

3.3 **Sample Duplicate:** A duplicate is analyzed for every 20 samples to verify the method precision.

3.4 **Matrix Spike:** A specific aliquot of sample into which a known amount of analyte is added. The analytical spike is analyzed with the sample batch and the percent recovery is calculated in order to assess the matrix effect on the analytical system.

3.5 **C_5 through C_8 Aliphatic Hydrocarbons:** are defined as all aliphatic hydrocarbon compounds which elute on the chromatogram from n-pentane (C_5) to just before n-nonane (C_9).

3.6 **C_9 through C_{12} Aliphatic Hydrocarbons:** are defined as all aliphatic hydrocarbon compounds which elute on the chromatogram from n-nonane (C_9) to just before naphthalene.

3.7 **C_9 through C_{10} Aromatic Hydrocarbons:** are defined as all aromatic hydrocarbon compounds which elute on the 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.

3.8 **Target VPH Analytes:** are defined as benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, naphthalene, and methyl-tert-butylether.

3.9 **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.

3.10 **Volatile Petroleum Hydrocarbon (VPH) Component Standard:** is defined as a 13 component mixture of the aliphatic and aromatic compounds listed in Table 2. 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 the 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.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

4.1 All samples must be iced or refrigerated at $4^{\circ}C \pm 2^{\circ}C$ from the time of collection until analysis.

4.2 Aqueous sample collection is done by our clients using 40mL pre-washed and pre- preserved glass vials. The sampler is instructed to fill the vial so it is completely full to the point of a positive meniscus but not overflowing without any air bubbles. A Teflon-sealed cap is then screwed tight onto the vial. The vial is inverted to insure that there are no air bubbles. A triplicate sampling is always done so that another vial of the same sample is available for analysis in case one of the following occurs:

4.2.1 The sample dilution has to be made.
4.2.2 There's an air bubble in the vial.
4.2.3 The vial is broken in transport.

4.3 All VPH aqueous samples **must** be analyzed within 14 days of collection and **should** be field preserved with 1:1 HCl to a pH<2.

4.4 All aqueous samples are pH checked after analysis. The pH results are documented in the injection run logs for each sample. All samples analyzed for VPH must have a pH<2. If the pH>2, then the data is flagged and noted in the case narrative.

4.5 **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 sampling devices, (encore samplers) provided that the samples are extruded and preserved in methanol within 48 hours of collection.

4.6 The desired ratio of methanol-to-soil is 1mL 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. A recommended practice is for a laboratory to provide to a field sampling technician labeled, pre-weighed sampling vials with a measured volume of methanol, and a scribed marked indicating the level of methanol that should exist in the vial when the required quantity of soil sample has been added. This requires an estimate on the density and moisture content of the soil sample; a good estimate for most soils is 10-15 mL of displaced volume for 20 grams soil. **In all cases, the soil sample in the vial must be completely covered by methanol.**

4.7 The laboratory prepares VPH VOA vials as follows:

4.7.1 20mL of purge and trap grade methanol is measured out into 40ml VOA vials, spiked with 40µL of a VOA surrogate mix at 1,250 ng/µL for a final concentration of 2,500ug/L, weighed, recorded, and marked to approximate the 20g addition of soil, and sent out in duplicate for sample collection.

4.7.2 The VOA vials are returned with about 20g of soil in each sample vial. The sample VOA vials are re-weighed to determine sample weight. One methanol vial is sent out as a trip blank with each project.

4.8 VPH soil samples have a 28 day holding time starting at the time of collection.

5.0 POTENTIAL PROBLEMS AND INTERFERENCES

It is important to be able to demonstrate that analytical results are not biased by laboratory contamination. The GC/MS operator is responsible for taking the following precautions.

5.1 GLASSWARE and SYRINGES:

5.1.1 All glassware and syringes used in the preparation of volatile organic standards or samples are thoroughly cleaned before each use.

5.1.2 Syringes for transferring methanol based standards are rinsed with methanol a minimum of three times before each use. Syringes for samples and aqueous standards are rinsed with methanol and then three times with distilled volatile-free water before each use.

5.1.3 Volumetric flasks and other glassware used in the preparation of samples or standards are rinsed with methanol and then three times with distilled water for aqueous based samples and standards or three times with methanol for methanol standards.

5.2 PURGE and TRAP UNITS Tekmar LSC 2000,Tekmar LSC 3000, O-I 4560, and Dynatech Dynatrap

The Purge and trap unit can be a source of contamination in volatile organic samples.
To minimize the possibility of this occurring, the following steps are taken.

5.2.1 The Tekmar LSC 2000, 3000 and autosampler automatically drains the sample out after purging and bakes out the trap at 225°C for 8 minutes while purging helium through the purging chamber. The autosampler rinses its syringe with distilled water and also flushes the purge lines and purge chamber twice during the bake cycle.

5.2.2 The sample analyses are examined before running the instrument the next day. If a sample contains high amounts of analytes, the next sample is examined to see if it contains any of the analytes. If there is any possibility of analytes carrying over from the previous sample, the sample(s) following are re-analyzed.

5.2.3 Method blanks are analyzed daily and must meet acceptance criteria before samples are analyzed.

5.2.4 Occasionally, the purging chamber is cleaned with soap and water and then rinsed.

5.3 CONTAMINATION FROM OTHER SOURCES:

5.3.1 Organic compounds such as chlorinated solvents, ketones, and ethers can be identified and integrated using the MS detector and noted in the case narrative that the range contains non-petroleum hydrocarbon.

5.3.2 Trip blanks are analyzed with samples to check for contamination. Trip blanks are provided by laboratory and are analyzed to check for contamination by diffusion of volatile organics through the septum seal of the sample container into the sample during shipment and storage.

5.3.3 Volatile organic sampling vials may be contaminated. Vials supplied by AMRO have been purchased pre-cleaned from a reputable supplier that uses the EPA protocol to clean their vials. AMRO policy does not allow re-use of volatile organic sampling vials.

5.3.4 Refrigerator blanks are used to determine contamination of the refrigerators. Refrigerator Water and Methanol blanks are analyzed monthly and evaluated to determine if there are any analytes detected that exceed the reporting limits. Any hits are investigated to determine the source of the contamination. Data will be reviewed by QC and kept on file by the VOA department.

5.4 MATRIX INTERFERENCE:

5.4.1 Sometimes, when a sample is analyzed, it foams, or contains compounds that interfere with the internal standards or surrogates. Such a sample is not re-analyzed except at a dilution due to potential harm to the instruments. It is considered to be due to matrix interference and the data is flagged and listed in the case narrative.

5.4.2 Soil samples with a high content of moisture due to either low % solids or very large sample weight may have low surrogate recoveries . This matrix effect is caused by the water in the sample diluting the methanol and surrogates.

6.0 HEALTH AND SAFETY

6.1 AMRO has a laboratory safety program in place that applies to all employees. There is a safety officer as well as employees with 40 hours of OSHA training. The air quality of the laboratory has been monitored and employees are sent for physicals. All employees receive fire and safety training upon employment.

6.2 Fire extinguishers are located in various areas of the lab. A lab evacuation plan is posted in every room, with a designated meeting place.

6.3 All new analysts receive training on the safe handling of samples, standards, the changing of gas cylinders, and the operation of instruments. In the lab, clean laboratory coats and gloves are worn when working with samples. Neat standards are made up in hoods. When gas tanks are replaced, the carrier with chain is used properly, and all gas tanks are chained in place. Soap is used to check for any leaks.

6.4 Care is taken with glassware and syringes to prevent injury. Broken glass and syringes are promptly removed to broken glass containers. First aid kits are available throughout the lab. There are also eyewash stations and an emergency shower.

6.5 MSDS's are reviewed for each chemical used to ensure proper precautions are observed when handling chemicals.

6.6 Pollution prevention – The use of chemical exhaust hood are required when working with chemicals. They are specifically designed to minimize analyst exposure. The hood exhaust is monitored periodically to ensure environmental exposure is minimized.

6.7 Waste control – AMRO takes whatever steps possible to minimize waste. This includes volume reduction where appropriate. AMRO also properly segregates wastes according to contaminants and a commercial vendor is utilized for waste disposal.

7.0 INSTRUMENTS AND EQUIPMENT

7.1 Hewlett Packard 5890 GC/MS and 6890 Gas Chromatographs with 5971, 5972 and 5973 Mass Selective Detectors. They are equipped with purge and trap units, auto samplers, and data systems with the following software: Hewlett Packard DOS Chemstation for data acquisition, and Enviroquant for data processing, including the NBS 54K Library or NIST 74K Library of Mass Spectra. Columns used for each instrument are listed in section 9.1.

7.2 Edwards Vacuum Pump

7.3 Balance: Analytical 0.0001g

7.4 Gas Tight Syringes: 10, 25, 50, 100, 250, 500, 1,000uL, 5, 10, or 25 mL with manufacturer tolerances of ±1%.

7.5 Class A volumetric flasks: 1, 2, 5, 10, 25, 50, 100, 250, 500, &1,000mL

7.6 Stainless steel spatulas

7.7 Glass disposable pipets.

7.8 Pre-cleaned 40mL VOA vials with Teflon Septum and screw caps.

8.0 REAGENTS AND STANDARDS

8.1 AMRO VOA reagent water – Reverse Osmosis/Granular Activated Carbon (RO/GAC) Water from a Culligan System. Method Blanks are used to monitor contaminant levels of volatile analytes. Reagent water is used for making up daily standards, dilutions, water blanks, and rinsing flasks and syringes.

8.2 Methanol, purge and trap grade, from Burdick and Jackson is used for making up standards, prepping VPH VOA vials, and rinsing syringes.

8.3 1:1 Hydrochloric Acid (HCl) for preservation.

8.4 Stock solutions of standards:

8.4.1 Both stock and working standards in methanol are stored in the freezer. Daily standards are made up in water, stored without headspace, and are discarded after each day of use.

8.4.2 Good laboratory procedure for making up standards is as follows:

8.4.2.1 All syringes and volumetric flasks are rinsed three times with methanol.

8.4.2.2 Syringe needles are wiped with Kimwipes and air dried by pumping the plunger up and down several times.

8.4.2.3 The volumetric flask is filled with methanol as high as possible, leaving room for the addition of the standard.

8.4.2.4 The standard is drawn up in the syringe above the desired level, inverted to allow any air bubble to rise to the needle, and the plunger is pushed to the correct amount.

8.4.2.5 The needle is wiped with a Kimwipe and the needle is placed into the flask, preferably under the methanol and the plunger is pushed down gently to avoid purging.

8.4.2.6 If the needle can not reach the methanol, even with tilting the flask, then it should be eluted slowly down the side of the glass.

8.4.3 Initial and CCV calibration stock standards: Used within six months after ampule opening unless otherwise indicated:

8.4.3.1 VPH standard obtained from Accustandard contains the following target analytes and alkanes.

Table 2. Volatile Petroleum Hydrocarbon (VPH) 13 Component Standard

Component	Concentrations, µg/µL
Pentane	10
2-Methyl pentane	15
Methyl-t-butylether	15
2,2,4-Trimethylpentane	15
Benzene	5
Toluene	15
Nonane	10
Ethylbenzene	5
m-Xylene	10
p-Xylene	10
o-Xylene	10
1,2,4-Trimethylbenzene	10
Naphthalene	10

8.4.5 Stock Quality Control check standards (used for LCS): Used within six months after ampule opening unless otherwise indicated.

8.4.5.1 Accustandard VPH spike mix containing MTBE, benzene, toluene, ethylbenzene, xylenes, and napththalene at 5,000ng/µL.

8.4.5.2 8260B Internal Standard obtained from Restek, contains Fluorobenzene, Chlorobenzene-d5, 1,4 Dichlorobenzene-d4 at 2,500 ng/µL.

8.4.5.3 8260B surrogate solution is obtained from Restek and contains 1,2-Dichloroethane-d4, Toluene-d8, p-Bromofluorobenzene, Dibromofluoromethane at 2,500 ng/µL.

8.4.5.4 4-Bromofluorobenzene (BFB) from Supleco at concentration 2,000 ng/µL used to tune instruments. Used within three months.

8.5 Working standards:

The working standards are good for one month unless otherwise indicated. Initial and daily calibration working standards mix is prepared by adding 50ul of the VPH component mix into a 5mL volumetric flask and transferring it to a 5mL vial with a teflon liner. Store in the freezer at all times.

8.5.1 Quality control check standards (LCS)– good one month unless otherwise specified.

8.5.1.1 VPH Spike Mix- Add 200ul of stock to 2mL volumetric with methanol for a final concentration of 500 ng/µL.

8.5.1.2 IS/Surrogate solution

Instrument V1a
480µL of 8260 IS Mix to 10 mL in methanol. Final concentration 120ng/µL.

Instrument V2
500µL of 8260 IS Mix to 10 mL in methanol. Final concentration 125ng/µL.

Instrument V3
360µL of 8260 IS Mix , 8260 SS Mix ,and 180ul of 2,5-DBT to 10 mL in methanol. Final concentration 90ng/µL.

Instrument V4
Soil - 480uL of 8260 IS Mix to 10 mL in methanol.
Final concentration 120ng/µL.
Water – 400uL of 8260 IS Mix , 8260 SS Mix and 200ul of 2,5 DBT to 10mL in methanol. Final concentration 100ng/µL.

8.6 BFB

8.6.1 125µL stock to 10 mL in methanol, final concentration 25ng/µL.

8.7 Surrogate Calibration Working Solution

8.7.1 500µL of Restek 8260B surrogate stock solution plus 250µL of Accustandard DBT stock solution into 5mL of methanol, for a final concentration of 250µg/mL.

8.7.2 Daily Standards are made up daily in VOA reagent water. All standards for extracted soil calibration or calibration verification are made in reagent water with 4% methanol added. Surrogates and Internal Standards are added by the autosampler for all water and low level soil standards.

8.8 Initial Calibration Standards

8.8.1 1, 5, 10, 25, and 50µL of the working solution, plus 40µL of the surrogate spike mix in 4mls of methanol when calibrating for soils; into 100mL of reagent water to prepare the 1, 5, 10, 25, and 50µg/L aqueous and soil standards, respectively. To prepare the 75, 100, 200, and 300µg/L aqueous standards, add 37.5, 50, 100, and 150µL of the combined working solution, plus 15, 10, 5, and 2µL respectively of the surrogate spike mix in 2mls of methanol when calibrating for soils, into 50mL of reagent water.

8.9 Daily calibration verification standards

8.9.1 LCS: 20µL of the VPH LCS spike mix at 500ng/µL into a VPH prepped vial containing 20mls of methanol for a concentration of 500ng/mL.

8.9.2 BFB: 40 µL working standard solution to 100 mL DI, final concentration 10ng/mL.

8.10 Tracking of Analytical Standards

8.10.1 Chemical Receipt

The receipt of all standards, neat compounds and reagents from commercial sources is documented in the Chemical Receiving Logbook by sample receiving personnel or designate. Each solution or compound is assigned a unique standard receipt ID number, the letter "A" and a four digit sequential number. The date received, source, lot number, expiration date and disposal date are recorded. The expiration dates are provided from the manufacturer and the disposal dates are completed by AMRO employees when standards are used up or disposed.

8.11 Standards Preparation

Standards are prepared as written in the respective SOPs. In order to assure the accuracy of standards the following general guidelines are used:

8.11.1 AMRO purchases pesticide residue grade solvents and purge and trap grade Methanol for organic standard preparation and organic sample extractions.

8.11.2 ACS reagent grade chemicals are used when the method warrants.

8.11.3 Any stock standards that are purchased are accompanied by a certificate of analysis from the manufacturer.

8.11.4 Class A volumetric glassware is used to prepare standards.

8.12 Standard Tracking

It is important to be able to track all analytical standards back to their sources. The following procedure is used by AMRO personnel to accomplish this:

Organic Standard Tracking - The Organic Standards Tracking Log consists of three sections plus an ID index. The ID index assures that no two standards are assigned the same ID number.

8.12.1 Stock Section: Whenever a stock standard solution is opened or is prepared from a neat compound, this information is recorded in the Stock Standard Logbook section of the standard tracking log. The stock solution is assigned a new ID number consisting of the date of preparation plus a letter suffix starting with the letter "A". This ID

along with the compound name, concentration and initials of the person making the stock are included on the label. Stock standards are good one year from the date prepared or the date provided by manufacturer, whichever is shorter. Example - The fourth volatile standard prepared on April 15, 1989 would have the standard ID V041589D. This number will be recorded in the logbook and written on the container.

8.12.2 Working Section: Whenever a working standard solution opened or is prepared, whether from AMRO stocks or commercially obtained stocks, the information is recorded in the Working Standard section of the standard tracking log. The solution is assigned a new ID number based on the date it is prepared plus a letter suffix. This number along with a descriptive name, concentration (or conc. varied) and the initials of the person preparing the solution are included on the label. The expiration of working standards vary depending on the use. Standards should be used in accordance with method specifications and manufacturer's instructions.

8.13 Standard Storage

Standards and reagents are stored per method specifications and manufacturer's instructions. Volatile standards are stored in a freezer at minus 10°C to 20°C.

8.14 Solvent Check Analysis

All extraction procedures are performed using pesticide residue grade solvents and a method blank analysis is performed when a new lot number is received to verify the absence of target analytes.

9.0 GC/MS PROCEDURE

9.1 Instrument Conditions and Settings

9.1.1 GC/MS (V-1A): HP-624 25 m x 0.2 mm ID column 35°C for 5 min., 8°C/min to 195°C, hold for 4 min. for a total of 29 min. analyzed time Tekmar LSC 3000 purge and trap Dynatech PTA-30w/s Autosampler Supelco Trap E

9.1.2 GC/MS (V-2): HP-624 25m x 0.2mm ID column 35°C for 5 min., 8°C/min to 195°C, hold for 4 min. for a total of 29 min. analyzed time

Tekmar LSC 2000 purge and trap Dynatech Archon w/s autosampler.
Supelco Trap E

9.1.3 GC/MS (V-3): HP-624 25m x 0.2mm ID column 35°C for 5 min., 8°C/min to 195°C, hold for 4 min. for a total of 29 mins analyzed time
Dynatrap Purge Trap E Dynatech Precision Sampling Dynatrap Autosampler.

9.1.4 GC/MS (V-4): RTX-624 20m x 0.18 mm ID column35°C for 4 min., 10°C /min to 195°C, hold for 3 min. for a total of 23 min. analyzed time. 4560 OI Sample Concentrator and Archon autosampler.

9.1.5 All systems have a capillary injection port, operating in the split mode.

9.1.6 V1A, V3 and V4 have Water Management Systems with a 150°C Bake, 100°C Purge and 50°C Desorb.

9.1.7 Settings:

Purge gas - helium grade 99.995	Desorb Flow - 30 mL/min
Purge time - 11 minutes	Desorb Time - 4 min at 200°C
Purge flow - 25-30 mL/min	Bake Time - 8 min at 225°C

Tekmar valve and transfer line temp - 105°C
Injection port temp - 225°C
Detector temp - 160-180°C
Transfer line temp - 280°C
Split Ratio 30:1

Purge temp. – ambient for all Dynatrap/Tekmar 2000 AS. 25°C for V4 (O.T. 4560), and 40°C for all low level bisulfate preserved soils.

V-4 has an Electronic Pressure Control – constant flow 0.5 mL/min.

Chromatographic Column: The required column is: 105M x 0.53 mm I.D. Restek RTX 502.2 with 3 micron film thickness, or column with equivalent chromatographic properties.

NOTE: Based upon data obtained from the Round Robin testing programs, the choice of chromatographic column may have a significant impact on the apportionment and quantitation of aliphatic and aromatic compounds within the fractional ranges specified in this method. Substitution of the required column is not

allowed, unless it can be demonstrated that the selected column has equivalent chromatographic properties and retention times for the aliphatic and aromatic compounds and ranges of interest.

To demonstrate equivalency of column chromatography, a neat gasoline standard must be analyzed on both the required column and the proposed substitute column, with all other run and system parameters held constant. The concentrations of C_5 - C_8 and C_9 - C_{12} Aliphatic Hydrocarbons must be determined for each column (in which the concentration of the Target/aromatic analytes have been subtracted from the GC/FID response). The Relative Percent Difference between the concentrations of each fraction obtained for each column, must be equal to or less than 25%.

The laboratory uses a HP-624 25m x 0.2mm capillary column (or equivalent). A longer column to achieve separation is not necessary for a MS detector. A gasoline TIC study(identifies each compound and its retention time), suggested by the DEP was run to validate our column choice. Weathered gasoline was also analyzed with excellent recoveries. The MDL studies, where certified gasoline is analyzed at low levels and the VPH method must be capable of producing total recoveries of 70% to 130%, supports our method modification.

9.2 Initial Demonstration of Capabilities

It is important to be able to demonstrate that all sample analyses were performed in an 'in-control' manner. It is the responsibility of the GC/MS operator to perform the following procedures prior to sample analysis.

9.2.1 Initial Demonstration of Lab Performance

The ability of AMRO to produce accurate and precise data is demonstrated per instrument/per analyst for each method. This information was entered on an Excel® spreadsheet and is kept on file with the QC department along with the associated chromatograms and quantitation output pages. It consists of an Initial Calibration (IC) for all target analytes, Initial Calibration Verification (ICV) for all target analytes, a Method Detection Limit Study (MDL) and Precision and Accuracy Study (P&A) for each analyte, each instrument and each matrix on an annual basis.

9.2.2 MDL

The method detection limit is defined in 40 CFR 136 Appendix B. The MDL is determined annually by the analysis of a minimum of seven

replicate samples, all containing an analyte(s) of the same low-level concentration. These replicate samples are put through all the preparation steps that a sample is put through. The standard deviation of the results of these analyses is multiplied by the appropriate student T-test value and the resulting value is deemed the method detection limit for that specific analyte.

MDL studies of each analyte must be reported annually for each instrument, column, matrix, and extraction method. To ensure that reasonable MDL values are determined, an MDL check sample is analyzed by spiking an interference free matrix with all target analytes at about two times the determined MDL. The MDL check sample is taken through the same process as the MDL. If any of the target analytes are not detected, the MDL study is modified and repeated until the MDL check sample is detectable. The MDL check will be analyzed quarterly and after major instrument maintenance or changes in the instrumentation or instrumental conditions to verify sensitivity of the method. For VPH analysis, the MDL check sample corresponds to the lowest level standard analyzed in the calibration curve (below the reporting limit)

MDL studies for the hydrocarbon ranges

MDL studies for the hydrocarbon ranges are preformed by analyzing 7-10 replicates of a certified gasoline reference standard at the lowest level possible and still achieve the required recoveries. Generally, this is a 250ug/L or (6.25mg/Kg) gasoline reference standard.

The mean recovery of the summation of (unadjusted) C_5 - C_8 and C_9 - C_{12} Aliphatic Hydrocarbons (i.e., the entire GC/FID chromatogram), expressed as a percentage of the true value of the gasoline reference standard, must be between 70% and 130%. For each hydrocarbon range, the %RSD must be less than or equal to 25%.

MDL studies for the target analytes

MDL studies for the target analytes are preformed by analyzing 7-10 replicates of the VPH standard at the lowest calibration standard level. For each analyte, excluding naphthalene and n-nonane, the mean accuracy expressed as a percentage of the true value, must be between 70% and 130%. For each analyte, the %RSD of replicate samples must be less than or equal to 25%.

9.2.3 Precision &Accuracy

9.2.3.1 Accuracy is a measure of the degree to which the analytical result approaches the "true" value of the concentration of the analyte being determined. Precision in the laboratory is determined by the comparison of duplicates, where duplicate samples result from an original sample that has been split for identical analyses. Precision and Accuracy in the laboratory is assessed initially by the analyses of a minimum of 4 replicate samples at a mid-level point of the expected range. The percent recoveries and Relative Standard Deviations (RSD) are evaluated and compared to method specifications or default limits where applicable.

9.2.3.2 For each VPH target analyte, the mean accuracy, expressed as a percentage of the true value must be between 70% and 130%, and the %RSD must be less than or equal to 25%. Lower recoveries are permissible for naphthalene and n-nonane.

9.2.3.3 The regular analysis of known standards such as the Laboratory Control Samples (LCS), and matrix and analytical spikes also assess accuracy. Accuracy within the laboratory is expressed in terms of percent recovery. The precision of data is regularly evaluated by determining the relative percent difference (RPD) of duplicate (replicate) analyses.

9.3 Tuning

The mass spectrometer must be verified to be in tune, has adequate sensitivity, is standardizing for the compounds of interest, and is demonstrating that the system is free of interferences. Calibration begins with the analysis of Bromofluorobenzene (BFB). This performance test must be passed before any samples, blanks, or standards are analyzed. The calibration is good for 24hrs from the injection time of the BFB for VPH samples.

9.3.1 **Tuning** - 50 ng of BFB (40 µL of a 25ng/µL solution is added to 100 mL of VOA free water) and 5 mL is purged for 11 minutes and desorbed onto the chromatographic column. The analysis is performed at 100°C to 150°C. A scan delay of two to five minutes is used. After the scan delay, data is acquired for five to ten minutes. The expected elution time of the BFB is six to eight minutes from the start of data acquisition. The background corrected average of three scans at the apex or of an average across the peak is checked against the tuning requirements in Table 1. One simple subtraction of background is required within twenty scans of the left side of the

peak. There is a procedure file program in the software that will locate and check the BFB for a passing spectrum in the manner explained above. This procedure will be used routinely to eliminate any subjectivity from the tuning process. If this procedure fails to produce ion abundances that meet the criteria, it will display the message "no passing spectrum found in data file: xxxxx" on the printer. If this occurs the BFB must be re-analyzed. If repeated analyses fail to produce acceptable results, then the instrument must be manually tuned according to the Hewlett-Packard reference manual. If the tune does not meet criteria, a single scan option can be used. This should not be required on a routine basis. If it does become necessary, consult with the section head. Once an acceptable tune is obtained, the following items are documented in the analyzed log:

9.3.1.1 The scan number(s) of the good tune and background corrections used to achieve it.

9.3.1.2 The time of injection.

9.3.1.3 Once a good spectrum is found a hardcopy of the following information is filed in the daily calibration file.

9.3.1.4 The following is the BFB tune criteria:

Table 3
BFB Mass - Intensity Specifications

Mass	Intensity Required (relative abundance)
50	15 to 40% of Mass 95
75	30 to 60% of Mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of Mass 95
173	Less than 2% of Mass 174
174	Greater than 50% of Mass 95
175	5 to 9% of Mass 174
176	Greater than 95% but less than 101% of Mass 174
177	5 to 9% of Mass 176

9.4 Initial Calibration Procedure

A multi-level calibration consisting of 1, 2, 5, 10, 25, 50, 100, 200, 300, 500µg/L is performed using standards obtained commercially. The three internal standards that are used: Fluorobenzene, Chlorobenzene-d5, and 1,4 Dichlorobenzene-d4 at a level of 25.0µg/L.

9.4.1 The RRF (Relative Response Factor) is calculated as follows:

$$RRF = \frac{(Ax \times Cis)}{(Ais \times Cx)}$$

where: Ax = Area of the characteristic ion for the compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cis = Concentration of the specific internal standard.
Cx = Concentration of the compound being measured.

The hydrocarbon ranges are integrated as follows:

M/z 43 C5-C8 aliphatic: from 0.1 minutes before n-pentane to just at the unslope before n-nonane

M/z 43 C9-C12 aliphatic: from just at the unslope before nonane to 0.1 minutes before naphthalene

M/z 91 C9-C10 aromatic: from just after o-Xylene to 0.1 minutes before naphthalene

The response factors for the ranges are calculated using an internal standard at 25µg/L.

Area of Range / Area of IS x conc. IS (25µg/L)/ ppb range

= range response factor

The ppb of the range is calculated by summing the concentrations of the alkane components of the VPH standard that are within the range and are detected by the MS using the specified ion. Method blanks, internal standards, and surrogates need not to be subtracted as they contribute a negligible amount of area. BTEX compounds are not subtracted as they are not detected using ion 43.

The 43 ion contribution from MTBE is added to the VPH standard's C5-C8 concentration. MTBE peaks in samples are integrated for ion 43 and subtracted from the area of the C5-C8 range.

The average RRF and % Relative Standard Deviation (%RSD) must be calculated for each compound and range using the 8-10 RRF values calculated for each compound from the initial (8-10 point) calibration curve.

If the % RSD of any compound is less than or equal to 20%, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

If the % RSD of any compound is 20% or greater, construct calibration curves of area ratio (A / Ais) versus concentration ratio (Cx/ Cis) using first order (Linear Regression) or second order (Quadratic Regression) regression fit of the initial calibration points. The requirement for Linear Regression correlation coefficient is greater than 0.990. If the Linear Regression criteria is not met, then Quadratic equation (second order) may be used with a minimum of 6 data points. In either case, the curve must be printed and stored in the file with the initial calibration to document evaluation. The analyst should select the regression order, which introduces the least calibration error into the quantitation and minimizes the y-intercept value (constant term).

Linear and Quadratic Regressions each have several options available in the software. The analyst must chose which order will be used. Options available are equal weighting, inverse of conc., and inverse square of conc.. The analyst should choose the curve order and weighting which gives the best coefficient of the determination (COD) and a y-intercept nearest to the origin, given the calibration blank is clean.

The analyst may drop the lowest or highest point for an analyte, possibly requiring either a change in reporting limits or narrowing the calibration range. An entire level may be deleted if there is cause to believe there was a poor injection, etc. The section head should examine the calibration to ensure the proper procedures were followed.

9.5 GC/MS Daily Calibration Procedure:

9.5.1 Daily Calibration Check:

9.5.1.1 The VPH standard (continuing calibration at 50ppb but varied periodically) is analyzed daily to verify the calibration curve. Each analyte and hydrocarbon range must be within 25%(%Drift) to pass.

% Drift = c1 - c2/c1 x 100

where: c1 is the analyte or range concentration
c2 is the standard concentration

9.5.1.2 The internal standards must be monitored for retention time and area of response. The internal standard area of the daily standard may not vary by more than - 50% or + 200% and their retention times by ±30 seconds from the comparable standard in the initial calibration. The samples should also be monitored for internal standard area and retention time and any falling outside the criteria with regard to either the initial calibration or the daily passing standard should be examined to determine if there is any impact on the data and if so then they are re-analyzed.

9.5.1.3 If a standard does not pass it may be analyzed again, but if it fails the second time, the system should be checked for problems and corrected.

9.5.1.4 New initial calibrations are always analyzed after major system changes such as replacing filaments, cleaning the source, significant re-tuning of the mass spectrometer, significant changes in purge & trap conditions, etc.

9.5.1.6 Laboratory Control Sample : A LCS is prepared using 100µL in 50ml DI of a 10ng/µL secondary source standard. For soil LCS, 2 mL Methanol, 100µL of 10 ng/µL second Source standard mix in 50 ml DI is used.

9.5.1.7 If any of the target analytes of the LCS do not meet acceptance criteria , within 70% to 130% recovery , the LCS may be re-analyzed. If the acceptance criteria are still not met the system is checked for problems and corrected before samples are analyzed.

9.5.2 Blank analysis:

A 5 mL aliquot of volatile free laboratory water is analyzed in the same manner as standards and samples to demonstrate that the system is interference free for water samples. For soil samples, the method blank contains 200ul of methanol and surrogates per 5 mL purge as do the standards and samples. When this has been demonstrated sample analysis may begin. A hardcopy of the blank chromatogram and quant output page is filed with the daily calibration data. The blank should not contain any analyte above one half the reporting limit. If there are any analytes over the reporting limit the blank must be re-analyzed before any samples are analyzed.

10.0 SAMPLE PROCEDURE

10.1 Preparation of Samples

Once the calibration procedure has been successfully completed the analysis of actual samples may begin. It is the responsibility of the GC/MS operator to follow these procedures. To determine which samples need to be analyzed on a given day, a daily work list is printed and used by the analyst to know when the analysis needs to be completed to satisfy the preservation / holding time requirements and the client's requests.

10.1.1 Preserved aqueous samples must be analyzed within 14 days from date of sampling. The pH must be <2.

10.1.2 In general, water samples are analyzed at 5 mL unless there is a known history of contamination in the sample or some matrix problem which requires a dilution to be analyzed. For a dilution of 1:10, 5mls of sample is removed with a gastight syringe and added to a 50ml volumetric flask containing distilled water. VOA Reagent water is added to the 50mL mark, capped, the volumetric is inverted three times, and poured gently into a VOA vial for analysis.The Dynatrap and the Archon Autosamplers are capable of performing a 1:10 dilution directly from a VOA vial placed in the tray for sample analysis.

10.1.2.1 All water samples, standards and blanks are spiked with internal standards and surrogate standards at 25µg/L prior to analysis by the instrument.

10.1.2.2 Allow samples to come to room temperature.

10.1.2.3 Aqueous samples are checked the day after analysis with low range pH paper to ensure it was preserved to a pH <2 at the time of collection. If pH is >2, the duplicate vials are checked to determine if one has a pH<2. If a vial is found, the sample is re-analyzed. Otherwise, it is noted in the case narrative.

10.1.3 VPH Soil samples

10.1.3.1 VPH soils are extracted on-site using the VOA vials containing methanol with surrogates that were prepared in the laboratory. Soil vials are weighed and the final vial weights and soil sample weights are recorded in the VPH soil prep logbook. The soil samples have been in the methanol from one to several days and require only stirring to obtain a thorough extraction as evidenced by analysis at later dates. SW-846 Methods 8260B and 5035B require only stirring and no longer suggest sonication as it invariably heat to the VOA vials and may result in loss of volatiles. However if a client requests sonication it will be done.

10.1.4 Soil method blank and LCS

10.1.4.1 Methanol blanks and a LCS are prepared each day soils are analyzed. 20 mls of methanol is added to a VOA vial and spiked with 40ul of surrogate mix. Twenty grams of sand may be used with the methanol blank and LCS if a client requests it, otherwise SW-846 Methods 8260B and 5035B are followed (in-house extractions of samples are prohibited) The LCS also has 100µl of the QC mix containing the VPH target compounds added upon dilution into a 50ml volumetric.

10.1.5 Soil matrix spike

10.1.5.1 For every twenty soil samples a spike and spike duplicate are prepared by spiking 100ul of a 10ng/ul mix in to a 50ml volumetric containing 2mls of a methanol extraction prepared in the laboratory. Normally, SW-846 Methods 8260B and 5035B are followed in the soil preparation of VPH matrix spikes. However some clients may prefer direct spiking of a duplicate soil vial despite possible associated problems.

10.1.5.2 Soil samples must be extracted and analyzed within 28 days from the date of collection. Encore samplers soil contents must be preserved in methanol within 48 hours of sampling and analyzed within 28 days from collection

10.2 Analysis of Samples

10.2.1 Every analytical batch of samples requires the following:

- BFB TUNE
- VPH STANDARD (at 50ppb usually but concentration varied)
- LABORATORY CONTROL SAMPLE (LCS) – 20 µg/L
- PROCEDURAL(METHOD) BLANK
- SAMPLES
- DUPLICATE SAMPLE-each 20 samples
- MS/MSD- For every 20 client samples a spike and spike duplicate is required. They are spiked by AMRO with the LCS spike containing the 7 VPH target compounds. 100µl of a 10ng/µl mix is added to a 50ml volumetric containing 10mls of a water sample. Samples must be selected for spiking at random and rotated among clients and sites from batch to batch. In some cases, the client may specify which sample is to used for MS/MSD; if not , the laboratory shall pick a representative sample based on the following:

  A. MS/MSD shall not be performed on Trip Blank, Rinsate Blank or Field Blank.
  B. Adequate sample weight/volume.
  C. Client requested QC deliverables.

10.2.2 Samples and standards are introduced to the GC/MS System using 40mL VOA vials, which are put into the autosampler tray. The autosampler syringe delivers 5mL to the purging chamber along with the internal standards and surrogates (the autosampler is equipped with a syringe or vial, which the operator fills with the internal standard and surrogate mix for waters). Also, a 40mL VOA vial containing Bromofluorobenzene (BFB) at a concentration of 50ng/5mL is placed on the tray for tuning (no SS is added).

10.2.3 Check the reservoir for water.

10.2.4 Check the IS and SS vials.

10.2.5 Type in the sequence of samples into the computer.

10.2.6 Recheck the vials in the autosampler to make sure they match the typed sequence.

10.2.7 Check the Helium.

10.2.8 Helium purges through the chamber and the volatile analytes are absorbed on the trap, a tube containing an OV-1/Tenax/Silica Gel/Charcoal mixture. After purging is complete, the trap is heated and backflushed with helium to desorb the compounds. The analytes are carried along a heated transfer line to the GC inlet, where the glass liner meets the narrow bore capillary column. At this point the analytes are heated, mixed and split. The column is temperature programmed to separate the analytes and is interfaced by a Mass Spectrometer for detection.

10.2.9 The raw data will print from the instrument as each sample is running.

10.3 Evaluation of Results

10.3.1 Identification of Compounds (Qualification)

Carefully evaluate the EICP and sample to reference spectrum match for each hit above or near the reporting limit that is detected by the data system. The qualitative identification of compounds is based on retention time and on the comparison of the sample mass spectrum, after background subtraction,

with characteristic ions in a reference mass spectrum. The characteristic ions are the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than 3 such ions occur in the reference spectrum. Compounds are identified as being present if:

- The intensities of the characteristic ions of a compound maximize in the same scan within one scan of each other.

- The relative retention time of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

- The relative intensities of the characteristic ions agree within 20% of the relative intensities of those ions in the reference spectrum.

10.3.1.1 All VPH target isomers are reported individually, with the exception of m- and p-xylene, which co-elute and are reported as an isomer sum.

10.3.1.2 Print a hardcopy of the graphics display In QEDIT for all confirmed positive results in client samples. Make certain the reference and sample spectra are included, as well as the properly displayed EICP.

10.4 Quantitation of Compounds

The identified compound will be quantitated based on its response compared to that of its internal standard.

10.4.1 When the mass spectrometer is linear, the concentration of each analyte in the sample is, for water samples:

$$\text{Concentration } \mu g/L = \frac{(Ax)(Is)(5mL)}{(Ais)(RF)(Vo)}$$

Ax = area of characteristic ion for compound or range being measured
Is = amount of internal standard injected (ng)
Ais = area of characteristic ion for internal standard
RF = mean relative response factor for compound being measured
Vo = volume of water purged in mL.

10.4.2 The integration of compounds for standards and samples should be performed to be in the same manner as the initial calibration integration. Cases where the initial calibration is in question should be investigated to ensure it is not related to poor maintenance, damaged or defective column, or other issues, which should be solved before further analysis.

10.4.3 The following must be checked for each compound present in standards and samples to ensure proper integration has been performed.

- The peak shape of the calibration compound must be maintained for standards and samples. This should take into account any shouldering, peak tailing, and peak co-elution.

- The EICP retention time windows for each compound of the calibration must be applied to standards and samples. If there is a retention time shift confirmed by comparison of the Internal Standards and Surrogates then carefully examine each EICP for potential target shifts. Watch especially in the narrow retention time windows where a shift might cause all or part of a peak to leave the window and be missed or mis-integrated by the data system. If false negatives due to retention time shifting appear likely then the sample must be reanalyzed.

- The baseline integration techniques for each compound of the calibration must be maintained for the standards and the samples. This should take into account elevated baselines, column compensation corrections and negative peaks in samples.

- Make sure that positive identification of compounds has been established through EICP's and all method requirements have been met.

- Ensure any positive results are within the lower and upper levels of the calibration curve and above the reporting limits for each compound. All positive results above the calibration curve must be reanalyzed in dilution.

10.4.4 If there are any cases where the integration or spectral identification of a compound is questionable after ensuring the above steps have been followed then consult another qualified analyst. "Before" and "After" chromatograms and spectra should be printed in these cases, dated and initialed by the analyst and the qualified consultant.

10.4.5 Analytes with initial calibration RRFs >20 %RSD are fitted to a linear regression or quadratic regression in the initial calibration. The software will automatically quantitiate the analyte by the parameters set for the initial calibration, average response, linear regression or quadratic regression.

10.4.6 Once all the data has been evaluated it is submitted for data review. The following must be submitted for each project:

10.4.7.1 The raw data from the instrument that was printed while the sample was running. This consists of the quantitiation report and the chromatograms.

10.4.7.2 The data after it has been reviewed by the analyst. This consists of the quantitiation report that was reviewed.

10.4.7.3 A copy of the injection log(s) associated with the samples for the project.

10.4.7.4 Copies of the preparation sheets associated with the samples.

10.4.7.5 A copy of the applicable blanks if the

project is a Level 2 package or higher. See the Quality Systems Manual for Package Levels.

10.4.7.6 If the project is a Level 4 or 5, copies of the following items must be provided to data review: Initial Calibration summary and raw data along with the information described in sections 10.4.7.1 to 10.4.7.5 are required.

10.4.7.7 The GC/MS Checklist (Attachment 2) is completed by the analyst. The checklist provides an overview of the issues associated with the data. Any items that do not meet acceptable criteria must be qualified by the analyst in the form of a documented investigation of the issue(s) written on the narrative form.

11.0 INSTRUMENT PREVENTATIVE MAINTENANCE AND REPAIR

Instrument maintenance and repair records are maintained to document satisfactory instrument performance. The operator is generally responsible to see that records are well kept. Records of major maintenance and repair are kept in the instrument maintenance log per instrument. Routine maintenance procedures such as changing the GC septum need only be recorded in the instrument analysis log.

11.1 Daily maintenance procedures:

The following items should be checked on every day that an instrument is used for analysis.

11.1.1 Trap and column performance. This is monitored by checking the response factor of key compounds, which indicate trap and column degradation and observing column bleed. Change trap or column if necessary.

11.1.2 Check that gases have adequate supply to last until the following day. Change tanks if necessary.

11.1.3 Check data file space and quant space.

11.2 Biweekly maintenance procedures:

The following items should be done every two weeks:

11.2.1 Check split flow on GC.

11.2.2 Check purge gas flow on the purge&trap. Adjust if necessary.

11.2.3 Check Teflon ferrules on purge&trap for wear. Replace if necessary.

11.2.4 Check Teflon purge lines on purge&trap for wear. Replace if necessary.

11.3 Three month maintenance procedure:

11.3.1 Every 3 months the o-rings, Teflon block should be replaced and intake filters should be vacuumed.

11.4 Six month maintenance procedure:

11.4.1 Every 6 months the vacuum pump oil should be changed.

11.5 Maintenance "As needed":

The following service should be performed when system performance indicates.

11.5.1 Clean the analyzer source. This will become necessary if a high background becomes apparent which is not attributable to column degradation or the system cannot meet BFB criteria.

11.5.2 Replace the electron multiplier when the maximum gain no longer provides the required sensitivity.

11.5.3 Replace the ion source filament as needed.

12.0 CALCULATIONS

12.1 Refer to Section 10.4

13.0 QUALITY CONTROL

A formal quality control program is in operation at the present time at AMRO. The Laboratory Control limits for surrogate, matrix spikes and laboratory control sample spike are updated on an annual basis.

13.1 Standards

13.1.1 The spiking solutions are obtained commercially. New lots of spiking solution are compared to the ones currently in use before being used. If they differ by more than 10%, then replace spike. If still out, new calibration curves will probably need to be prepared with the new solutions.

13.2 Internal standard

13.2.1 All samples, standards, and blanks are spiked with internal standards at 25 µg/l in water and soil extractions prior to analysis. Internal standard areas are monitored.

13.2.2 If examination of the total ion chromatogram shows no evidence of matrix interference or elevated baseline, the samples should be re-analyzed to determine if there is some other matrix effect behavior or that the added internal standard solution is no longer acceptable for use. If re-analysis exhibits the same behavior then the analyst will report the data and generate a Non-Conformance report with some assessment of data impact.

13.2.3 If examination of the total ion chromatogram shows evidence of matrix interference or elevated baseline, the analyst should evaluate whether a dilution is warranted due to peak distortion. If there are no chromatographic anomalies, the data is reported as is since the internal standard is designed to allow for some matrix effects or inlet discrimination.

13.3 Surrogates

13.3.1 All samples, standards, and blanks are spiked with surrogate standards at 25µg/l in water, and at 100µg/l in methanol preserved soils prior to analysis. Surrogate recoveries are monitored. Surrogate recoveries for VPH samples are fixed by the method at 70%-130%. If the surrogate recovery is outside of the upper acceptance limit and there is an assignable cause,

the data can be reported with a note of qualification. If the surrogate recovery is outside of the range and there is no assignable cause, the sample must be re-analyzed. If it is not possible to re-analyzed the samples due to hold time constraints, the data must be qualified.

13.4 Blanks

13.4.1 Blanks are analyzed daily. Blanks are evaluated to ensure analyte levels are below reporting limits. If any compounds are seen in blanks greater than the reporting limit, the system is checked for contamination, and the blank is re-analyzed. AMRO has observed Naphthalene presence in the blanks at levels below reporting limits due to carryover from the VPH Standard containing 100 ppb of Naphthalene. Analysis should not proceed if the initial blanks are greater than one half the reporting limit for any other analytes and the problem can be corrected by instrument adjustment or cleaning, e.g. analyzing additional blanks.

13.4.2 Trip blanks are analyzed along with the samples they arrived at the lab with. Their purpose is to assess the possibility of cross-contamination of the samples while in transport. If provided, they are analyzed with the samples they are used to assess.

13.4.3 Field blanks are also analyzed when they are provided by the client.

13.5 Laboratory Control Samples

13.5.1 Laboratory Control Samples (LCS) are prepared with samples and analyzed with the sample matrix they correspond to. The LCS for water contains all target analytes. *If LCS does not produce acceptable recoveries based on VPH limits then they are re-analyzed. If the LCS is still unacceptable, the LCS solution is checked, as well as the calibration. If the LCS is not acceptable the LCS is re-analyzed before any samples are run.*

13.6 Matrix Spikes

13.6.1 For aqueous and soil samples, a Matrix Spike (MS) and Matrix Spike Duplicate (MSD) must be analyzed with every 20 samples.

13.6.2 If the results of both matrix spike samples do not meet acceptance criteria then matrix interference is suspected. The Laboratory Control Sample (LCS) is reported to prove that the system is 'in-

control' and the spike results are suspected to be due to matrix interference, providing the LCS was acceptable.

13.7 Duplicates

13.7.1 The laboratory analyzes a sample duplicate, Matrix Spike (MS) and Matrix Spike Duplicate (MSD) with every analytical batch (maximum of 20 samples). The results are evaluated to ensure acceptable reproducibility for the analysis. The Relative Percent Difference (RPD) between the concentrations of the analysis are calculated as follows:

$$\%RPD = \frac{(\text{MS conc.} - \text{MSD conc})}{(\text{MS conc.} + \text{MSD conc.})/2)} * 100$$

$$\%RPD = \frac{(\text{sample conc.} - \text{sample dup conc})}{(\text{sample conc.} + \text{sample dup conc.})/2)} * 100$$

13.7.2 The %RPD must be ≤50% for the target analytes and hydrocarbon ranges in the sample duplicate.

13.7.3 The %RPD must be <25% for the target analytes in the MS and MSD. If the %RPD is not acceptable then an assignable cause such as sample non-homogeneity or carry over from a high sample, etc is explored. If a reasonable cause is found the batch is accepted, if not the MS and MSD are reanalyzed.

13.7 Corrective Action

13.8.1 Problems that are identified at the bench level and are corrected by the analysts are noted on the GC/MS Data Review Checklist, (Attachment 2). If any non-conformance is determined by lab manager review, a QC review or Corrective Action is to be included with the applicable report. Sections are informed of non-conformance issues in an effort to prevent reoccurrence. Any issues that are made evident by a client, resulting in corrective actions being completed which identify the issue, cause and correction. This information is provided to the client.

14.0 DATA REVIEW AND STORAGE

AMRO's goal for completeness is 100%. The following data calculating, reviewing and reporting procedures are followed to obtain that goal.

14.1 Data Review - performed by the analyst:

When an analysis of a sample is complete, the analysis for that sample should be checked and the data calculated as soon as possible to identify any problems while still within the holding time for the analysis. The following steps should be taken to ensure that a good analysis has been obtained.

14.1.1 Check that all calibration analyses associated with the sample meet criteria to ensure acceptance criteria is met.

14.1.2 Check the internal standard areas. They should be -50 to +200% of the I.S. areas in the Initial Calibration standard.

Check the surrogates for the required 70%-130% recovery for VPH samples.

14.1.4 Check the LCS to be sure the results are inside the limits, as well as the matrix spike and matrix spike duplicate results.

14.1.5 Check the analyzed times to be sure the tuning requirements are met.

14.1.6 Check that no compounds or ranges exceed the calibration range. If there are, these samples must be reanalyzed at a dilution.

14.1.7 Check the chromatography (good peak shape, baseline not noisy, good sensitivity).

14.1.8 Check the analysis for carryover or contamination. If any carryover is evident, these samples must be reanalyzed.

14.1.9 Check that the amount of sample analyzed is correctly recorded in the chromatogram header.

14.1.10 Check spectrum, area, and retention time of any positive hits on the quant output page.

14.1.11 Perform the final calculations on any positively identified compound in µg/L, taking into account dilution factors, etc.

Calculate the multiplier which equals grams of sample purged and write it on the quant output page. The soil multiplier is calculated by the following calculation:

$$\text{grams sample purged} = \frac{\text{sample wt. grams}}{\text{mL Methanol extracted}} \times \frac{\%\ \text{solids}}{100} \times \text{mL Methanol purged}$$

soil multiplier = 5mls purge/ g sample purged

14.1.12 Check the chromatogram for very large peaks not picked up by quant. If any are present, check the spectrum to be sure it is not a target compound that is over the calibration range or outside the normal retention time window. If not a target compound, make a note on the chromatogram that the peak is an unknown and use the library to identify if possible.

14.1.13 Check to see if there are any other analyses of the sample. If so, check to see if the data agrees.

Any problems discovered during this preliminary data check will necessitate re-analysis unless the lab manager authorizes use of the data in writing with an explanation of why the data is being used.

All calculations should be written in black ballpoint pen ink. All cross-outs should be a single line and should be initialed. The person performing these data calculations and checks should sign and date the bottom of the quant page.

14.2 Data Review - performed by the department supervisor or designate.

When all samples for a given project have been analyzed and the results have been calculated, the project goes through the following data review procedure:

14.2.1 The reviewer reads over all associated paperwork to become familiar with the requirements of the project.

14.2.2 The project is checked for completeness.

14.2.3 Data sheets are checked for accuracy.

14.2.4 The data calculations are spot-checked. If any problems are encountered then the whole package should be checked.

14.2.5 The QC data sheets are checked.

Any problems encountered by the reviewer are brought to the attention of the lab manager.

14.3 Data Reporting

14.3.1 Many report options are available to clients of AMRO. It is AMRO policy to discuss with all clients their reporting requirements soon after receipt of the samples. The cover letter for the data reports will address any quality control problems, either with the condition of the samples upon receipt or with the analyses, or contain a statement that no quality control problems were encountered. The letter will also contain a statement that it is an integral part of the data report.

14.3.2 The significant modifications of the MA DEP method are summarized in (Attachment 3).

14.3.3 The data elements in the required data reporting format (Appx. 3 of the MA DEP VPH method) are produced in AMRO's default VPH LIMS Report format (see Attachment 4).

14.4 Data Archival

14.4.1 GC/MS Data Files:

All raw GC/MS data files are archived through the Network and are backed up on a tape drive through the server.

14.4.2 Data Reports:

Final data and QC reports are input into Excel and spreadsheet files. Template files exist on the Network for final data reports, daily QC check reports, sample spike reports, initial precision and accuracy data, wastewater method accuracy data, surrogate recovery data, and MDL data. When data is input template files are renamed as follows:

data reports XXX#####

Where X 's are the first three characters of the AMRO client code and #'s are the AMRO project and sample number.

15.0 REFERENCES

15.1 40 CFR Part 136 Appendix B, 1984.

15.2 USEPA Office of Solid and Hazardous Waste - SW-846 Method Chapter 1, Rev. 1 7/92.

15.3 Massachusetts Departments of Environmental Protection-Method for the Determination of Volatile Petroleum Hydrocarbons (VPH), January 1998.

15.4 USEPA Office of Solid and Hazardous Waste - SW-846 Method 8000B, Rev. 2 12/96.

15.5 USEPA Office of Solid and Hazardous Waste - SW-846 Method 8260B, Rev. 2 12/96.

15.6 USEPA Office of Solid and Hazardous Waste - SW-846 Method 5030B, Rev. 2 12/96.

15.7 USEPA Office of Solid and Hazardous Waste - SW-846 Method 5035, Rev. 2 12/96.

15.8 New Jersey Department of Environmental Protection "Methodology for the Field Extraction/Preservation of Soil Samples with Methanol for Volatile Organic Compounds", 2/97.

15.9 USACE Shell for Analytical Chemistry Requirements, Version 1.0, Nov.2, 1998

Attachment 1

AMRO Environmental
Laboratories Corporation

111 Herrick Street
Merrimack, NH 03054
(603) 424-2022

QUALIFICATION CARD FOR METHOD MADEP-VPH

Trainee: _____ Signature: _____

Trainer: _____ Signature: _____

I. Knowledge Factors:

SOP Title: _____ Revision Number/Date: _____

1. Did the Trainee read and understand the above SOP?	Yes☐	No☐	NA☐
2. Was the Trainee instructed on how to properly fill out the documentation?	Yes☐	No☐	NA☐
3. Has the Trainee been instructed on the proper procedures for addressing potential problems?	Yes☐	No☐	NA☐

II. Practical Factors:

1. Has the Trainee completed a Precision and Accuracy Study?	Yes☐	No☐	NA☐
2. Has the Trainee completed an acceptable Performance Evaluation sample?	Yes☐	No☐	NA☐
3. Did the Trainee completed an acceptable Laboratory Control Sample (LCS)?	Yes☐	No☐	NA☐
4. Has the Trainee performed manual integration as indicated in the SOP?	Yes☐	No☐	NA☐

Completion Date: _____ Trainer's Signature: _____

I _____ have read, understood and follow the above method/SOP, which is in use at AMRO Laboratories for the analysis of samples under the National Environmental Laboratory Accreditation Program, have met the Demonstration of Capability.

Section Manager/ Supervisor: _____ Date: _____

QA Manager: _____ Date: _____

qc/qcmemos/forms/VPHqualcard Rev. 0 04/01

Attachment 2

AMRO Environmental
Laboratories Corporation

111 Herrick Street
Merrimack, NH 03054
(603) 424-2022

GC AND GC/MS DATA REVIEW CHECKLIST

LAB ORDER: _____ **CLIENT:** _____

Method:	**Sample(s) No.:**
Analysis:	**Matrix:**

A.	**GENERAL**			
1.	Copy of Prep/Extraction Log?	Y	N	NA
2.	Copy of Instrument Run Log or Tune List?	Y	N	NA
3.	Copy of dry weight log present?	Y	N	NA
4.	Are all sample checked for preservation after VOA analysis?	Y	N	NA
5.	All samples met extraction and/or analysis holding time criteria?	Y	N	NA
6.	Did the Tune pass and DFTPP or BFB injected every 12 hours?	Y	N	NA
7.	Are the surrogate recoveries for each sample within the QC limits?	Y	N	NA
8.	Method Blank- contaminant free?	Y	N	NA
9.	Initial Calibration meets method criteria for all compounds reported?	Y	N	NA
10.	Continuing Calibration meets method criteria for all compounds reported?	Y	N	NA
11.	Are all reported results within calibration range?	Y	N	NA
12.	LCS % Recovery criteria met for all compounds?	Y	N	NA
13.	MS/MSD %R's and %RPD's are met for all compounds?	Y	N	NA
14.	%RPD criteria met between sample and duplicate?	Y	N	NA
15.	Samples checked for carry over from sample to sample due to target or nontarget overload?	Y	N	NA
16.	Are all data exported to LIMS, calculated and verified?	Y	N	NA

COMMENTS

Analyst (s) _____ DATE: _____

REVIEWER: _____ DATE OF REVIEW: _____

qc/qcmemos/Forms/gcmschecklist Rev. 1 04/00

Attachment 3

AMRO Environmental Laboratories Corporation
111 Herrick Street
Merrimack, NH 03054

Volatile Petroleum Hydrocarbons (VPH)
Massachusetts Department of Environmental Protection (MADEP)
Method 1.0 - January 1998
AMRO Modifications

This modification is based on the use of a purge and trap gas chromatography mass spectrometer (GC/MS) system to analyze samples for VPH. The hydrocarbon ranges are quantified using predominant mass fragmentation ions which are characteristic for the range being measured. This approach eliminates potential false positives for the target analytes while providing accurate hydrocarbon range data.

The chromatographic column is an HP-624 capillary column which has been validated by GC/MS analysis of a gasoline standard to correctly identify the marker compounds and elution order of specific gasoline components. Batch quality control includes, at a minimum, method blank, laboratory control sample, and duplicate analysis. A matrix spike and/or matrix spike duplicate is analyzed if sufficient sample is submitted to the laboratory.

The Reporting Limit (RL) of this method for each of the collective aliphatic and aromatic ranges is approximately 0.6-2.8 mg/kg in soil and 25-110 µg/L in water. The RL of this method for the target analytes ranges from approximately 0.05-0.13 mg/kg in soil and 2.0-5.0 µg/L for water samples.

Extractable Petroleum Hydrocarbons (EPH)
Massachusetts Department of Environmental Protection (MADEP)
Method 1.0 - January 1998
AMRO Modifications

This modification is based on a solvent extraction and gas chromatography mass spectrometer (GC/MS) analysis. The hydrocarbon ranges are quantified using predominant mass fragmentation ions which are characteristic for the range being measured. This approach eliminates the silica gel solid-phase fractionation step. False positives for targeted PAH analytes are eliminated by using GC/MS as the primary analysis technique.

The chromatographic column is a J&W Scientific DB-5ms capillary column.
Internal standard calibration is performed using 5α-Androstane at a concentration of 40 ng/µL. o-Terphenyl and 1-Chlorooctadecane are added as surrogate compounds at 20 ng/µL in the sample extract. These two surrogates monitor the effects of the sample matrix and extraction efficiency. Two additional surrogates, 2-Fluorobiphenyl and 2-Bromonaphthalene, are added to the finished extract prior to analysis to monitor instrument performance. Batch quality control includes, at a minimum, a procedure blank, laboratory control sample and duplicate sample analysis. A matrix spike is analyzed if sufficient sample is submitted to the laboratory.

The Reporting Limit (RL) of this method for each of the collective aliphatic and aromatic ranges is approximately 2-15 mg/kg in soil and 10-50 µg/L in water. The RL of this method for the Target PAH analytes ranges from approximately 0.25 to 0.5mg/kg in soil; 1.0µg/L for water when operating the GC/MS in full scan mode, and 0.1 to 1.0µg/L when operating the GC/MS in SIM mode. For sites requiring the lowest levels cited in the Massachusetts Contingency Plan for water, GC/MS in the Selected Ion Monitoring (SIM) mode is used.

Attachment 4

AMRO Environmental Laboratories Corp.

Date: *05-Apr-01*

CLIENT: Client Sample ID:
Lab Order: Tag Number:
Project: Collection Date:
Lab ID: Matrix:

Analyses	Result	RL	Qual	Units	DF	Date Analyzed
VOLATILE PETROLEUM HYDROCARBONS		MAVPH				Analyst: SK
C5-C8 Aliphatic Hydrocarbons	410	100		µg/L	1	3/29/01 7:49:00 PM
C9-C12 Aliphatic Hydrocarbons	480	25		µg/L	1	3/29/01 7:49:00 PM
C9-C10 Aromatic Hydrocarbons	4,100	250		µg/L	10	3/30/01 11:27:00 AM
Methyl tert-butyl ether	ND	2.0		µg/L	1	3/29/01 7:49:00 PM
Benzene	77	2.0		µg/L	1	3/29/01 7:49:00 PM
Toluene	1,900	20		µg/L	10	3/30/01 11:27:00 AM
Ethylbenzene	630	20		µg/L	10	3/30/01 11:27:00 AM
m,p-Xylene	3,200	20		µg/L	10	3/30/01 11:27:00 AM
o-Xylene	1,600	20		µg/L	10	3/30/01 11:27:00 AM
Naphthalene	310	5.0		µg/L	1	3/29/01 7:49:00 PM
Surr: 1,2-Dichloroethane-d4	84.8	70-130		%REC	1	3/29/01 7:49:00 PM
Surr: 2,5-Dibromotoluene	125	70-130		%REC	1	3/29/01 7:49:00 PM
Surr: 4-Bromofluorobenzene	97.6	70-130		%REC	1	3/29/01 7:49:00 PM
Surr: Dibromofluoromethane	86.0	70-130		%REC	1	3/29/01 7:49:00 PM
Surr: Toluene-d8	123	70-130		%REC	1	3/29/01 7:49:00 PM

Hydrocarbon range data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range. EPH: C11-C22 Aromatic Hydrocarbons exclude the concentration of target PAH analytes. VPH: C5-C8 Aliphatic Hydrocarbons exclude the concentration of target analytes eluting in this range. C9-C12 Aliphatic Hydrocarbons exclude the concentration of target analytes eluting in this range and concentration of C9-C10 Aromatic Hydrocarbons.

CERTIFICATION

Were all QA/QC procedures required by the VPH or EPH method followed: ___ Yes ___ No - If No, See Case Narrative

Were all performance/acceptance standards for required QA/QC procedures achieved: ___ Yes ___ No - If No, See Case Narrative

Were any significant modifications made to the method as specified in section 11.3: ___ No ___ Yes - Details enclosed

I attest under the pains and penalties of perjury that, based upon my inquiry of those individuals immediately responsible for obtaining the information, the material contained in this report is, to the best of my knowledge and belief, accurate and complete.

SIGNATURE: _____ DATE: _____

PRINTED NAME: Nancy Stewart POSITION: Laboratory Director (or designee)

Qualifiers: RL - Reporting Limit; defined as the lowest concentration the laboratory can accurately quantitate.

ND - Not Detected at the Reporting Limit S - Spike Recovery outside accepted recovery limits E - Value above quantitation range

J - Analyte detected below quantitation limits R - RPD outside accepted recovery limits # - See Case Narrative

B - Analyte detected in the associated Method Blank H - Method prescribed holding time exceeded

AMRO Environmental
Laboratories Corporation

111 Herrick Street
Merrimack, NH 03054
(603) 424-2022

INTERIM CHANGE NOTIFICATION

SOP Number:
SOP Tittle: Method for the Determination of Extractable Petroleum Hydrcarbons (EPH) Modified for GC/MS Analysis

Revision Number: 1
Revision Date: 9/20/01

10.5.9 Use a linear regression calibration (with a forced origin) if the RSD of any analyte exceeds 25% in the IC. Linear regression (with a forced origin) is recommended for the ranges to provide better high range quantitation and prevent false negatives on blanks and cleaner client samples. Never use quadratic calibration for the ranges because the data system is unable to quantify areas exceeding the high standard even if within the peak height defined linear range. Delete the high standard point if necessary to achieve the linearity requirements in Sec.10.2.3 of the EPH method. Quadratic regressions with a forced origin may be used for single target analytes if it provides the best curve fit and adequate quantitation over the calibration range. The minimum correlation coefficient for linear regressions is 0.99. The minimum coefficient of deviation for quadratic regressions is 0.99.

Approvals

Section Supervisor/ Manager — Date: 09 2001

QA Manager — Date: 09/20/01

AMRO Environmental Laboratories Corporation

111 Herrick Street, Merrimack, NH 03054
TEL: (603) 424-2022 · FAX: (603) 429-8496

METHOD FOR THE DETERMINATION

OF EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)

Modified for GC/MS Analysis

Revision No.: 1

Revision Date: 04/06/2001

Prepared By: _____ Date: 04-11-01

Approved By: _____ Date: 04-11-01
SVO Supervisor

Approved By: _____ Date: 04-11-01
Organic Manager

Approved By: _____ Date: 04-11-01
Laboratory Director

Approved By: _____ Date: 04-11-01
Quality Assurance Manager

TABLE OF CONTENTS

1.0 SCOPE and APPLICATION

1.1 This method is designed to measure the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil. Extractable aliphatic hydrocarbons are collectively quantitated within two ranges: C_9 through C_{18}, and C_{19} through C_{36}. Extractable aromatic hydrocarbons are collectively quantitated within the C_{11} through C_{22} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150 °C and 500 °C.

1.2 AMRO performs this method based on solvent extraction without silica gel fractionation and gas chromatograph/mass spectrometry (GC/MS) analysis using a Mass Selective detector. The common fragment ions characteristic of the low mass alkyl series (m/z 43, 57, and 71) plus the low mass ion of the monocycloparaffins series (m/z 67) are used to quantify the aliphatic hydrocarbons (See Additional References 1,2,and 3). The additional ions added in this revision, especially m/z 67, improve the quantitation of the unresolved components (UCM) in distillate fuels such as diesel and lube oil. The common ring fragment ions of the aromatic low mass series (m/z 50, 63, and 74) are used to quantify the aromatic hydrocarbons (See Additional References 1,2, and 3). The additional ions added in this revision improve the sensitivity of method for the relatively low abundance ring fragment ions. The particular ions chosen minimize interference between the aromatic and aliphatic compounds.

1.3 This method is designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MADEP, 1994). It is intended to generate data in a format suitable for evaluation by that approach, and generate data that may be compared to reporting and cleanup standards promulgated in the Massachusetts Contingency Plan (310 CMR 40.0000).

1.4 This method is also able to measure the individual concentrations of Target Polynuclear Aromatic Hydrocarbons (PAH) Analytes, including Diesel PAH Analytes, in water and soil. The use of this method to quantitate these analytes is optional, and the Method Detection Limits for some of these PAH compounds in water are greater than the notification and/or cleanup standards specified in the Massachusetts Contingency Plan for sites located in drinking water resources areas. In cases where it is necessary to demonstrate compliance with these standards, the use of a GC/MS method in the SIM mode may be necessary.

1.5 Petroleum products suitable for evaluation by this method include kerosene, fuel oil #2, fuel oil #4, fuel oil #6, diesel fuel, jet fuel, and certain lubricating oils. This method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, or other petroleum products which contain a significant percentage of hydrocarbons lighter than C_9. This method, in and of itself, is also not suitable for the evaluation of petroleum products which contain a significant percentage of hydrocarbons heavier than C_{36}.

1.6 The laboratory method Reporting Limit (RL) for each of the aliphatic and aromatic ranges is approximately 50mg/kg in soil and 100ug/L in water. The RL of this method for the target Polynuclear Aromatic Hydrocarbon (PAH) analytes is approximately 0.25 mg/kg in soil, 1ug/L in water in full scan mode, and 0.1ug/L in Selective Ion Monitoring (SIM) mode.

1.7 This method includes a data adjustment step to subtract the concentration of target analytes from the concentration of C_{11} through C_{22} Aromatic Hydrocarbons.

1.8 False positives for target PAH analytes are virtually eliminated by using full scan GC/MS as the analytical technique. SIM data for PAH analyte concentrations below 1µg/L introduces a small risk of false positives, however due to the dominance and high mass (relative to interferences) of the PAH molecular ions, this risk in most water samples is minimal. A small bias against late eluting non-target aromatic range compounds is introduced due to the lower relative abundance of the aromatic low mass series ions in higher molecular weight PAHs and alkylated PAHs.

1.9 Elimination of the fractionation step from this modified method eliminates the significant inherent bias against naphthalene and alkylnaphthalene recoveries in the aromatics fraction due to premature elution in the aliphatic fraction and also eliminates false positives for the aromatic range due to carryover into the aromatic fraction of aliphatic hydrocarbons in highly contaminated samples. Analytical precision is also dramatically improved due to the elimination of the highly variable results of fractionation under slightly different preparation conditions.

1.10 The method modification is compliant with the performance based requirements in Section 1.10 of the default MA DEP method. All required documentation is maintained and available for review in the laboratory. A synopsis of these methods modifications is attached to every data report form (see Attachment 3) and the "significant modifications" box is checked 'yes' in the certifications section of all reports.

1.11 Additional information and details on the MADEP VPH/EPH approach, and the results of inter-laboratory "Round Robin" evaluations of the MA DEP EPH method, are available at http://www.magnet.state.ma.us/dep/bwsc/pubs.htm. A complete copy of the MA DEP default EPH method with all AMRO GC/MS method modifications explicitly detailed in red italics is available as EPH-SOP98wAMROmod.doc

2.0 METHOD SUMMARY

2.1 A sample submitted for EPH analysis is extracted with methylene chloride, dried over sodium sulfate, and concentrated in a Turbovap or Kuderna-Danish apparatus. Solvent exchange and sample cleanup using silica gel cartridges is not necessary due to the selection of specific quantitation ions which characterize each hydrocarbon range. Extracted ion data for the target PAHs eliminates aliphatic hydrocarbon interferences. A single extract in methylene chloride with a final volume of 1mL for waters and 5mL for soils is prepared for analysis. The resultant EICP chromatogram of aliphatic compounds is collectively integrated within the C_9 through C_{18} and C_{19} through C_{36} ranges. The resultant EICP chromatogram of aromatic compounds is collectively integrated within the C_{11} through C_{22} range. The method specified quantitation ions are used to identify and quantitate individual concentrations of Target PAH Analytes.

2.2 Calibration curves or relative response factors determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of C_9 through C_{18} and C_{19} through C_{36} aliphatic hydrocarbons. Calibration curves or relative response factor determined using a PAH standard mixture is used to calculate a collective C_{11} through C_{22} aromatic hydrocarbon concentration. Calibration curves or relative response factors determined for individual components of the PAH standard mixture are also used to calculate individual concentrations of reported Target PAH Analytes and unreported n-alkane analytes. All quantitation is performed using the internal standard technique.

2.3 This method is suitable for the analysis of waters, soils, and sediments. When the reporting limits required for the PAH Target analytes is below 1ug/L for water samples, such as when the MCP GW-1 limits must be met, then a separate SIM analysis of the EPH extract is required.

2.4 This method is based on (1)MA DEP " Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), January 1998; (2) USEPA Methods 3510C, 3541, and 8270C, SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition , 1986, including Update III; (3) ASTM Methods for Evaluating Solid Waste", 3rd Edition, 1986, including Update III; ASTM Method D2425-93

3.0 DEFINITIONS

3.1 **Aliphatic Hydrocarbon Standard:** is defined as a 14 component mixture of the normal alkanes listed in Table 1. The compounds comprising the Aliphatic Hydrocarbon Standard are used to (a) define and establish windows for the two aliphatic hydrocarbons ranges, and (b) determine average chromatographic response factors that can in turn be used to calculate the collective concentration of aliphatic hydrocarbons in environmental samples within those hydrocarbon ranges.

3.2 **Analytical Batch:** is defined as a group of field samples with similar matrices which 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.

3.3 **Aromatic Hydrocarbon Standard** is defined as a 17 component mixture of the polynuclear aromatic hydrocarbons (PAHs) listed in Table 2. The compounds comprising the Aromatic Hydrocarbon Standard are used to (a) define the individual retention times and chromatographic response factors for each of the PAH analytes listed in Table 2, (b) define and establish the window for the C_{11} through C_{22} Aromatic Hydrocarbon range, and (c) determine an average chromatographic response factor that can in turn be used to calculate the collective concentration of aromatic hydrocarbons in environmental samples within the C_{11} through C_{22} hydrocarbon range.

3.4 **C_9 through C_{18} Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting from n-nonane (n-C_9) to just before n-nonadecane (n-C_{19}).

3.5 **C_{19} through C_{36} Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting from n-nonadecane (n-C_{19}) through n-hexatriacontane (n-C_{36}).

3.6 **C_{11} through C_{22} Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting from naphthalene through Benzo(g,h,i)Perylene, excluding Target PAH Analytes.

3.7 **Calibration Check Standard** or **Calibration Verification Standard (CCV)** is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock standard solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.15 **Laboratory Method Blank** 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.

3.16 **Matrix Spiking Solution** is defined as a solution prepared independently from the calibration standards, containing known concentrations of method analytes.

3.17 **System Solvent Blank** is defined as an aliquot of a method solvent (e.g., hexane or methylene chloride, pesticide grade or better) that is directly injected into the GC system. The purpose of the System 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 system contaminants.

3.18 **Surrogate Standards** are compounds spiked into all samples, blanks, and matrix spikes to monitor the efficacy of sample extraction, chromatographic, and calibration systems.

3.19 **Target PAH Analytes** are defined as the 17 polynuclear aromatic hydrocarbon (PAH) compounds listed in Table 2.

3.20 **Total Petroleum Hydrocarbons (TPH)** are defined as the collective concentration of all hydrocarbon compounds eluting from n-nonane to n-hexatriacontane, excluding Target PAH Analytes. TPH is equivalent to the summation of C_9 through C_{18} Aliphatic Hydrocarbons, C_{19} through C_{36} Aliphatic Hydrocarbons, and C_{11} through C_{22} Aromatic Hydrocarbons.

3.21 **Unadjusted C_{11} through C_{22} Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting from naphthalene through Benzo(g,h,i)Perylene.

3.22 **Unadjusted TPH** is defined as the collective concentration of all hydrocarbon compounds eluting from n-nonane to n-hexatriacontane.

3.23 All other terms are as defined in SW-846, "Test Methods for Evaluating Solid Waste", USEPA, September, 1986, and as amended and updated.

Table 1. Aliphatic Hydrocarbon Standard

Carbon Number	Compound	Retention Time (min.)[1]
9	n-Nonane	4.03
10	n-Decane	5.15
12	n-Dodecane	7.53
14	n-Tetradecane	9.85
16	n-Hexadecane	11.94
18	n-Octadecane	13.82
19	n-Nonadecane	14.69
20	n-Eicosane	15.53
1-Chloro-octadecane (surrogate)		16.24
22	n-Docosane	17.08
24	n-Tetracosane	18.49
26	n-Hexacosane	19.80
28	n-Octacosane	21.03
30	n-Triacontane	22.16
36	n-Hexatriacontane	23.61

[1] Retention times are instrument/column/calibration specific and are specified in the data system quantitation method after each initial calibration. The actual retention times and MDLs vary slightly over time and are on file in the laboratory for each calibration and MDL study.

Table 2. Aromatic Hydrocarbon Standard/Target PAH Analytes

Compound	Retention Time (min.)[1]	MDL[2]	
		Water (µg/L)	Soil (mg/kg)
Naphthalene	7.52	0.104	0.0216
2-Methylnaphthalene	8.84	0.148	0.0209
Acenaphthylene	10.60	0.149	0.0180
Acenaphthene	10.96	0.158	0.0286
Fluorene	11.99	0.191	0.0262
Phenanthrene	13.91	0.119	0.0181
Anthracene	14.02	0.132	0.0184
Ortho-Terphenyl (surrogate)	14.70	NA	NA
Fluoranthene	16.30	0.130	0.0188
Pyrene	16.74	0.155	0.0195
Benzo(a)Anthracene	19.16	0.138	0.0268
Chrysene	19.23	0.162	0.0227
Benzo(b)Fluoranthene	21.17	0.133	0.0279
Benzo(k)Fluoranthene	21.23	0.224	0.0224
Benzo(a)Pyrene	21.72	0.109	0.0193
Indeno(1,2,3-cd)Pyrene	23.57	0.212	0.0664
Dibenzo(a,h)Anthracene	23.61	0.135	0.0355
Benzo(g,h,i)Perylene	24.04	0.113	0.0355

[1,2] Retention times are instrument/column/calibration specific and are specified in the data system quantitation method after each initial calibration. The actual retention times and MDLs vary slightly over time and are on file in the laboratory for each calibration and MDL study.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

Aqueous samples are collected in 1 liter amber glass bottles with Teflon-lined screw Caps:

4.1 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with Teflon-lined screw caps.

4.2 Aqueous samples must be preserved at the time of sampling by the addition of a suitable acid to reduce the pH of the sample to less than 2.0. This may be accomplished by the addition of 5 mL of 1:1 HCl to a 1 liter sample. The use of alternative acids are permissible. Following collection and addition of acid, the sample must be cooled to 4°C.

4.3 Soil and sediment samples must be cooled to 4°C immediately after collection.

4.4 A chain of custody form must accompany all aqueous, soil and sediment samples, documenting the time and date of sampling and any preservative additions.

4.5 Aqueous samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

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

4.7 A summary of sample collection, preservation, and holding times is provided in Table 3.

Table 3. Holding Times and Preservatives for EPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	1-Liter amber glass bottle with Teflon-lined screw cap	Add 5 mL of 1:1 HCl; cool to 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days
Soil/Sediments Samples	4-oz. (120 mL) wide mouth amber glass jar with Teflon-lined screw cap	Cool to 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days

5.0 POTENTIAL PROBLEMS AND INTERFERENCES

5.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, followed by a DI water rinse, then acetone, and methylene chloride.

5.2 High purity reagents must be used to minimize interference problems.

5.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is analyzed, it must be followed by the analysis of a system solvent blank to check for cross-contamination.

5.4 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interference will vary considerably from one source to another depending upon the nature and diversity of the site being sampled. Many matrix interferences are eliminated by the use of specific ion GC/MS analysis, however some non-petroleum compounds can cause reportable concentrations for the hydrocarbon ranges. See Sec.5.6 below.

5.5 Certain organic compounds not associated with releases of petroleum products, including chlorinated hydrocarbons, phenols, and phthalate esters, will be quantitated as Extractable and Total Petroleum Hydrocarbons. If necessary and/or desirable, additional sample cleanup and/or analytical procedures may be employed to minimize or document the presence of such compounds.

5.6 Non-petroleum organic compounds will only contribute to the aromatic and aliphatic ranges if they possess the specific ions quantitated for each range. Mass spectral library searches can be used to tentatively identify non-petroleum compound peaks and semi-quantitatively estimate their individual concentration and contribution to the quantified ranges. Matrix interferences will occur if the interferent mass spectrum contains the range specific ions, e.g. phthalate esters will contribute to the C19-C36 Aliphatic Range and the C11-C22 Aromatic Range. If the aliphatic or aromatic range is dominated by non-petroleum compounds then the results report must be qualified appropriately in the narrative. If requested by a customer, exclusion of non-petroleum compounds from the reported range results must be clearly in the results report or narrative.

5.7 No fractionation is performed and loss of naphthalenes due to fractionation does not occur. Fractionation surrogates are added after extraction and before analysis to monitor matrix effects and post-extraction sample preparation.

6.0 HEALTH AND SAFETY

6.1 AMRO has a laboratory safety program in place that applies to all employees. There is a safety officer as well as employees with 40 hours of OSHA training. The air quality of the laboratory has been monitored and employees are sent for physicals. All employees receive fire and safety training upon employment.

6.2 Fire extinguishers are located in various areas of the lab. A lab evacuation plan is posted in every room, with a designated meeting place.

6.3 All new analysts receive training on the safe handling of samples, standards, the changing of gas cylinders, and the operation of instruments. In the lab, clean lab coats and gloves are worn when working with samples. Neat standards are made up in hoods. When gas tanks are replaced, the carrier with chain is used properly, and all gas tanks are chained in place. Soap is used to check for any leaks.

6.4 Care is taken with glassware and syringes to prevent injury. Broken glass and syringes are promptly removed to broken glass containers. First aid kits are available throughout the lab. There are also eyewash stations and an emergency shower.

6.5 MSDS's are reviewed for each chemical used to ensure proper precautions are observed when handling chemicals.

6.6 Pollution prevention: The use of chemical exhaust hood are required when working with chemicals. They are specifically designed to minimize analyst exposure. The hood exhaust is monitored periodically to ensure environmental exposure is minimized.

6.7 Waste Control: AMRO takes whatever steps possible to minimize waste. The elimination of the fractionation step in this GC/MS modified method significantly reduces solvent use and waste. AMRO also properly segregates wastes according to contaminants and a commercial vendor is utilized for waste disposal.

7.0 INSTRUMENTS AND EQUIPMENT

7.1 The following glassware is used for this method:

7.1.1 1-L amber glass bottles

7.1.2 4 oz. (120 mL) amber glass wide-mouth jars

7.1.3 Vials:

7.1.3.1 Auto sampler: 2-mL glass vials with Teflon-lined rubber crimp caps

7.1.3.2 5-mL vials with Teflon-lined caps

7.1.4 Glass funnels

7.1.5 2-L Separatory funnels with Teflon stopcock

7.1.6 Kuderna-Danish apparatus including 10-mL graduated concentrator tube, 500-mL Evaporative flask, & 3-ball Snyder column

7.1.7 250-mL Erlenmeyer flasks

7.1.8 Disposable pipets: Pasteur

7.1.9 25-mL graduated cylinder

7.1.10 1-Liter graduated cylinder

7.1.11 100-mL beakers

7.1.12 Class "A" volumetric flasks: 10, 25, 50 and 100-mL

7.1.13 Class "A" volumetric pipets: 1, 5 or 10-mL

7.1.14 Zymark TurboVap concentrator tubes

7.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

7.3 Zymark TurboVap or Organomation N-evap for sample concentration.

7.4 Water bath: Heated large beakers, capable of temperature control from hot Plates. The baths should be used under a hood.

7.5 Microsyringes: 10-µL, 100-µL, 250-µL, 500-µL, 1000-µL

7.6 Boiling Chips

7.7 O-I Analytical Soxtherm extraction apparatus

7.8 Drying oven

7.9 GC/MS:

7.9.1 GC/MS Data System: HP5971+HP5890GC (AMRO SV-1) HP5972+HP5890GC (AMRO SV-2 or 3), or HP5973+HP6890GC (AMRO SV-4).

7.9.2 J&W DB-5MS column 30M x 0.25mm, with 0.25µm film.

7.9.3 Auto sampler: The HP 7673 or 7673A or 6890 is used.

8.0 REAGENTS AND STANDARDS

8.1 Reagents

8.1.1 Reagent Water: organic free water (ASTM Type I reagent grade water).

8.1.2 Solvents: hexane, methylene chloride, and acetone; pesticide grade or better. Store away from other solvents.

8.1.3 Sodium sulfate: (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

8.1.4 Ottawa and/or masonry sand: free of extractable petroleum hydrocarbons.

8.2 Stock Standard and Working Calibration Solutions

Prepare stock standard solutions at approximately 1000 ng/µL, or purchase as certified solutions.

8.2.1 Aromatic Hydrocarbon Stock Standard:

The Aromatic Hydrocarbon Standard consists of the 17 PAH compounds listed in Table 2. Use Restek #31458 (1000µg/mL) or Accustandard #DRH-006S (1000µg/mL) for the PAHs.

8.2.2 Aliphatic Hydrocarbon Stock Standard:

The Aliphatic Hydrocarbon Standard consists of the 14 normal alkanes listed in Table 1. Use Restek #1459 (1000ug/mL) or Accustandard #DRH-007S (1000ug/mL) for the alkanes.

8.2.3 Petroleum Reference Standard:

The Petroleum Reference Standard consists of the neat EPA/API high aromatic fuel oil #2 reference material (WP 681) available from RTC (#954-020). This fuel is characterized with respect to total aromatic and total aliphatic hydrocarbon content. Prepare a stock solution by accurately weighing about 2.5g of reference fuel oil into 50mL of methylene chloride.

8.4.2 Fractionation Surrogate Spiking Solution:

The fractionation surrogate spike stock containing 4000µg/mL of 2-Bromonaphthalene and 2-Fluorobiphenyl (Restek #54363) which added at 5uL per mL of extract (25µL for soils, 5 µL for waters) immediately after extract concentration. Fractionation is not performed, therefore the fractionation surrogates are used to monitor the accuracy of the final volume amount of IS added, dilutions, and post-extraction matrix effects.

8.5 Internal Standard

8.5.1 The internal standard used is 5a-androstane. 1µL of 2000µg/mL spiking solution (Restek #31065) is added per 100uL of extract or diluted extract analyzed. Keep the IS vial away from heat and minimize the amount of time the miniert valve is open or screw cap is off to prevent evaporation of the solvent. Record the level of the meniscus on the vial with a marker after each use. Monitor this mark before using an opened vial to prevent errors due to over-concentrated IS.

8.5.2 When SIM analysis is performed the internal standard used is a 10X dilution of the IS mix used for BNA analysis (Supelco Cat. # 4-6955) which will contain the internal standards 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, and Perylene-d_{12} each at a concentration of 200ug/mL. 1uL of the IS is added for each 100uL of extract analyzed.

8.6 Matrix Spike Standard

8.6.1 Five or more analytes from each analyte group (i.e., aromatic and aliphatic hydrocarbons) are selected for use in a matrix spiking solution, which is prepared independently from the calibration standards.

8.6.2 The matrix spiking solution contains n-C9, n-C14, n-C19, n-C20, n-C28, naphthalene, acenaphthene, anthracene, pyrene, and chrysene at 25ug/mL in acetone which is prepared from stock Accustandard #DRH-MA-MS-40X-PAK (1000ug/mL) by adding 1.25mL of the stock to 50mL of acetone. Add 1mL of spiking solution to each soil or water or QC sample designated for spiking.

8.6.3 The samples selected as the matrix spike and laboratory control samples are fortified with 1.0 mL of the matrix spiking solution.

9.0 PROCEDURE

9.1 Sample Preparation

Samples are extracted using methylene chloride. The recommended extraction procedure for water samples is a separatory funnel liquid-liquid extraction technique based upon SW-846 Method 3510A. For soil or sediment samples, use of an automated Soxtherm extraction technique is used.

9.1.1 Water Extraction

9.1.1.1 Mark the meniscus on the 1 liter sample bottle (for later volume determination) and transfer it to a 2-liter separatory funnel. For blanks and quality control samples, pour 1 liter of reagent water into the separatory funnel. Add 1.0 mL of the surrogate spiking solution to all samples, blanks and matrix spikes. For samples selected for spiking, add 1.0 mL of the matrix spiking solution.

9.1.1.2 Check the pH of the sample with wide-range pH paper. Note the pH in the laboratory notebook. The pH of the sample need not be adjusted.

9.1.1.3 Add 60 mL methylene chloride to the sample bottle to rinse the inner walls of the container, then add this solvent to the separatory funnel.

9.1.1.4 Seal and shake the separatory funnel vigorously for 1 to 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once.

9.1.1.5 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask.

9.1.1.6 Repeat the extraction two more times using additional 60 mL portions of solvent. Combine the three solvent extracts in a 250-mL Erlenmeyer flask. (Steps 9.1.1.3 to 9.1.1.5)

9.1.1.7 For sample volume determination add water to the sample bottle to the level of the meniscus previously marked then transfer this water to a graduated cylinder.

9.1.1.8 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.1.9 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20 to 30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

9.1.1.10 Add one or two clean boiling chips to the K-D flask and attach a three ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 3-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.1.11 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the extract onto an air blowdown apparatus. Adjust the extract volume to 1 mL under a gentle stream of nitrogen or air. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher.

9.1.1.12 Add 5µL of the fractionation surrogate standard containing 20ng of each fractionation surrogate to the 1mL final extract volume. Carefully and thoroughly mix the sample extract after spiking because the spike solvent is hexane and it floats on the methylene chloride extract.

9.1.1.13 Record the AMRO solution ID numbers for all surrogate, matrix spike, and internal standards used to prepare the extracts for analysis.

9.1.1.14 The final extract volume is 1mL and no fractionation is performed before analysis.

9.1.2 Soil/Sediment Extraction using Soxtherm Extraction

9.1.2.1 Quickly weigh 20g of solid sample and then blend with 5 to 10g of NaSO4, sufficient amount to dry the sample, in a 250mL beaker. Transfer as soon as possible to the glass extraction thimble and add 1.0mL of surrogate spike solution, and 1.0mL of the matrix spike solution if needed.

9.1.2.2 Place 140 mL of methylene chloride into a Soxtherm beaker containing 1 or 2 boiling chips. Attach the beaker to the Soxtherm extractor and extract the sample for 4 hours.

9.1.2.3 Allow the extract to cool after the extraction is complete.

9.1.2.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask. Alternatively, sample concentration may be accomplished in the Turbovap concentrator.

9.1.2.5 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Wash the Soxtherm cup and sodium sulfate column with 100 to 125 mL of methylene chloride to complete the quantitative transfer.

9.1.2.6 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 3 to 2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.2.8 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Adjust the extract volume to 5 mL. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher.

9.1.2.9 Carefully add 25µL of the fractionation spike solution to the extract, transfer to a 5mL screw cap vial, seal and mix well. Mixing is critical because the fraction surrogate solvent is hexane which floats on the methylene chloride extract.

9.1.2.10 Record the sample preparation information for the extraction and concentration steps. At a minimum, record the date, sample laboratory number, sample volume, volume and concentration of added surrogates, fractionation surrogates, and matrix spike solutions, and any deviations or problems associated with the extraction of the samples.

9.1.2.11 An alternate concentration procedure is the Turbovap technique as described in the AMRO SOP for Automated Soxtherm Extraction, Sec. 7.12.1

9.1.2.12The final 5mL extract volume is not fractionated with silica gel.

9.1.3 Proceed with the analysis in accordance with Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.4 If chromatographic responses exceed the linear range of the system, dilute the aliphatic and/or aromatic extract(s) and re-analyze.

9.1.5 Determination of Percent Moisture

9.1.5.1 Soil and sediment sample results must be reported on a dry-weight basis. A portion of sample for moisture determination should be weighed out at the same time as the portion used for hydrocarbon determination.

9.1.5.2 Immediately after weighing a sample for extraction, transfer 5 to 10 g of the sample into a tared crucible. Dry this 5 to 10 g sample overnight at 105°C in an oven, and reweigh. Allow to cool in a desiccator before reweighing. Calculate the percent moisture of the sample using the equations provided in Section 11.4.

10.0 GC/MS PROCEDURE

10.1 Gas Chromatograph Conditions and Settings:

10.1.1 Temperature Program:
Initial Temp=50 °C, Initial Time = 1.70 min, Ramp#1= 35 °C/min to 100 °C, hold 1.00min., Ramp# 2=12 °C/min to 320 °C, hold 6.50 min

10.1.2 Interface Temperature: 300°C

10.1.3 Injection port temperature:280°C

10.1.4 GC operated in splitless mode

10.1.5 Column head pressure: Pressure pulse EPC in constant flow mode.

10.1.6 Gas Flows: The recommended carrier gas is helium. Carrier gas Flow: 1mL/min.

10.1.7 Sample/auto sampler injection is 2μL.

10.2 GC Maintenance:

10.2.1 Capillary columns: Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert.

10.2.2 Break off the first few inches, up to one foot if necessary, of the injection port side of the column to remove heavy non-volatile residues from the column head after dirty samples are analyzed.

10.2.3 Bake out the column at 300°C. Use the method COOKOUT to automatically clean out the heavy residues in the column at the end of each sequence. If these procedures fail to eliminate a column degradation or contamination problem, it may be necessary to replace the column.

10.3 Retention Time Windows:

10.3.1 Retention Time Windows are established by default at 0.2 min on either side of the peak apex in the Extracted Ion Current Profile (EICP) display.

10.3.2 The windows of closely eluting isomers are adjusted to optimize correct target detection by the data system. The isomer pairs that typically elute within the same window are:
(1) phenanthrene+anthracene, (2) benzo(a)antracene+chrysene, (3) benzo(b)fluoranthene+benzo(k)fluoranthene.

10.3.3 Statistical determination of the RT windows is not necessary due to the high reproducibility of retention times under the conditions specified above and because EICPs eliminate interferences from all but isomers with identical spectra. Update retention times whenever the peak apex moves from the center of the EICP window in the Initial Calibration (IC) or Calibration Verification (CV) data.

10.3.4 Place the C9-C18 range end and the C19-C36 range beginning at 0.01 min before the beginning of the **slope** of n-C19 in the EICP.
Place the end of the C19-C36 range 0.1 min after the end of the tail of n-C36. This assures the range markers are visible in the EICP and not lost in the n-C19 or n-C36 peaks.

10.3.5 EPH marker compounds and windows are summarized in Table 4.

Table 4. EPH Marker Compounds

Range/ Hydrocarbon Standard	Beginning Marker Compound	Ending Marker Compound
C_9-C_{18} Aliphatic Hydrocarbons	n-Nonane	Just Before n-Nonadecane
C_{19}-C_{36} Aliphatic Hydrocarbons	n-Nonadecane	n-Hexatriacontane
C_{11}-C_{22} Aromatic Hydrocarbons	Naphthalene	Benzo (g,h,i) Perylene

10.3.6 Retention time markers and scan start/stop times for the SIM analysis for PAHs are critical because proper window placement is required to detect the targets and if they fall outside the scan start/stop windows the sample must be reanalyzed. Typical scan windows are described in Table 5 below. Group start times are dependent on column length.

Table 5. SIM Target Groups

Group ID	Masses Scanned	Appx. Group Start Time	Target Analytes
1	152, 82	0.5min before[1]	1,4-Dichlorobezene-d4 (IS)[1], Nitrobenzene-5 (SS)
2	136, 128	0.6min before[2]	Naphthalene, Naphthalene-d8 (IS)[2]
3	142, 172	0.6min before[3]	2-Methylnaphthalene[3], 2-Fluorobiphenyl (SS)
4	152, 153, 164	0.4min before[4]	Acenaphthylene[4], Acenaphthene, Acenaphthene-d10 (IS)
5	166, 188, 178	0.4min before[5]	Fluorene[5], Phenanthrene-d10 (IS), Phenanthrene, Anthracene
6	202, 244	0.9min before[6]	Fluoranthene[6], Pyrene, Terphenyl-d14 (SS)
7	228, 240	0.9min before[7]	Benzo(a)anthracene[7], Chrysene, Chrysene-d12 (IS)
8	252, 264	0.8min before[8]	Benzo(b)fluoranthene[8], Benzo(k)fluoranthene, Benzo(a)pyrene, Perylene-d12 (IS)
9	278, 276	0.5min before[9]	Indeno(1,2,3-cd)pyrene[9], Dibenz(a,h)anthracene, Benzo(g,h,I)perylene

10.4 GC/MS Tuning:

10.4.1 The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP. Analyses must not begin until the tuning criteria are met.

Evaluate the whole peak average spectrum with a single scan background correction. A few scans across the peak apex or single background corrected scan may also be used to evaluate the tune. In either case, a hard copy showing the passing spectrum and passing criteria must be printed, dated and initialed by the analyst.

10.4.2 Use the DFTPP mass intensity criteria as tuning acceptance criteria.

MASS	ION ABUNDANCE CRITERIA
51	30.0-80.0 % of mass 198
68	< 2% of mass 69
69	0-200.0% of mass 198
70	< 2% of mass 69
127	25.0-75.0 % of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5.0-9.0 % of mass 198
255	0-200.0% of mass 198
275	10.0-30.0 % of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	40.0 – 110.0% of mass 198,
443	15.0-24.0 % of mass 442

NOTE: All subsequent standards, sample, MS/MSDs, and blanks associated With DFTPP analysis must use the identical mass spectrometer instrument conditions.

10.4.3 The hydrocarbon range calibration reliability is very dependent on the MS tune conditions. Attempt to match the DFTPP ion ratios for m/z 51, 255, and 442 as closely as possible between the tune run before an initial calibration and for each subsequent days DFTPP run prior to the daily CCV. Because the quant ion of the internal standard is a high mass (m/z 245) and the characteristic range ions are all low mass (m/z 43-71) the "tip" of the tune in DFTPP about the "fulcrum" of m/z 255 is critical. For example, if the response of m/z 51 tips up by 10% in DFTPP then the following CCV will probably show a high response for the ranges quantified against the IS. Adjusting the MS tune using calgas (FC-43) is quick way to correct for MS tune drift as the source becomes dirty and restore the CCVs to passing condition.

10.5 GC/MS Calibration Procedure

10.5.1 Listed below in Table 6 are the Calibration Standard Concentrations and the on-column masses for the ranges. The on-column concentration for each single target analyte is twice the solution concentration.

Table 6

Component	Conc. of standard analytes (ng/µL)					
	1	2.5	10	25	50	100
Total Mass C_9 - C_{18} Aliphatic Hydrocarbons, ng on-column (6 components)	12	30	120	300	600	1200
Total Mass C_{19} - C_{36} Aliphatic Hydrocarbons, ng on-column (8 components + 1 surrogate)	18	45	180	450	900	1800
Total Mass C_{11} - C_{22} Aromatic Hydrocarbons/ PAHs, ng on-column (17 components + 3 surrogates)	40	100	400	1000	2000	4000

10.5.2 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 2µL injections). Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each analyte. Alternatively, the ratio of the response to the amount injected, defined as the calibration factor (CF), may be calculated for method analytes at each standard concentration using Equation 1.

Equation 1: Calibration Factor

$$Calibration\ Factor\ (CF) = \frac{area\ of\ peak}{total\ mass\ injected\ (ng)}$$

If the percent relative standard deviation (%RSD) of the calibration factor is equal to or less than 25% over the working range for all analytes of interest, as determined using Equation 2, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

Equation 2: Percent Relative Standard Deviation

$$\%RSD = \frac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs} \times 100$$

10.5.3 A collective calibration curve or factor must also be established for each hydrocarbon range of interest. To calculate the collective CF for C_9-C_{18} Aliphatic Hydrocarbons, C_{19}-C_{36} Aliphatic Hydrocarbons, and C_{11}-C_{22} Aromatic Hydrocarbons, tabulate the summation of the peak areas of all components in that fraction (e.g., C_9-C_{18}, 6 components) against the total mass injected, using a forced baseline projection, and Equation 3. A listing of the collective concentrations of standards within each hydrocarbon range is provided in Table 5.

Surrogates with significant responses for the ions summed in the ranges are included in the initial and continuing calibration. Surrogate contribution is subtracted from the ranges for all samples.

Equation 3: Range Calibration Factor

$$Range\ CF = \frac{Total\ area\ of\ all\ component\ peaks}{Total\ mass\ injected\ (ng)}$$

10.5.4 The following initial calibration levels are employed for each component in the mixes: 1, 2.5, 10, 25, 50 and 100 ng/ uL. The IS is at 20ng/µL in each standard. Optimum linearity and sufficient sensitivity are achieved if the IS EICP area counts are around 100,000 for full scan MS. The initial calibration levels for EPH PAH analysis by SIM are 0.05, 0.2, 0.5, 2.0, 5, and 10 ug/mL. Note the calibration levels in the method are in on-column ng, not ug/L, so given the default 2uL injections the calibration levels are double the concentrations.

10.5.5 Inject each calibration standard using the same technique that will be applied to the samples (e.g., 2µL injection). Tabulate the peak height or peak area responses against the concentration of each compound and internal standard. Calculate relative response factors (RRF) for each individual compound using Equation 4.

Equation 4: Relative Response Factor

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the analyte to be measured.

C_{is} = Concentration of the internal standard, ng/µL.

A_{is} = Response for the internal standard.

C_s = Concentration of the analyte to be measured, ng/µL.

If the RF value over the working range is constant (≤ 25% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations.

10.5.6 A collective response factor must also be established for each hydrocarbon range of interest. To calculate the collective RFs for C_9-C_{18} Aliphatic Hydrocarbons, C_{19}-C_{36} Aliphatic Hydrocarbons, and C_{11} - C_{22} Aromatic Hydrocarbons, tabulate the summation of the peak areas of all components in that fraction (e.g., C_9-C_{18}, 6 components) against the total mass injected, using a forced baseline projection, and Equation 6. A listing of the collective concentrations of standards within each hydrocarbon range is provided in Table 4.

10.5.7 Surrogates with significant responses for the ions summed in the ranges are included in the initial and continuing calibration. Surrogate contribution is subtracted from the ranges for all samples.

Equation 5: Range Response Factor

$$Range\ RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Summation of peak areas of component standards (e.g., C_9-C_{18} Aliphatic Hydrocarbons, 6 components).

C_{is} = Concentration of internal standard, ng/µL.

A_{is} = Response for the internal standard.

C_s = Total mass concentration of injected standards, ng/µL. (See Table 5)

10.5.8 At a minimum, the RRF or calibration curve must be verified on each working day to verify instrument performance and linearity. If the percent drift for any reported target analyte varies from the predicted response by more than ± 25%, then a new calibration curve must be prepared for that analyte or range.

10.5.9 Use a linear regression calibration (with a forced origin) if the RSD of any analyte exceeds 25% in the IC. Linear regression (with a forced origin) is recommended for the ranges to provide better high range quantitation and prevent false negatives on blanks and cleaner client samples. Avoid quadratic calibrations for single analytes and never use quadratic calibration for the ranges because the data system is unable to quantify areas exceeding the high standard even if within the peak height defined linear range. Delete the high standard point if necessary to achieve the linearity requirements in Sec.10.2.3 of the EPH method. The minimum correlation coefficient for linear regressions is 0.99.

10.5.10 Upper linear range for non-target peaks in the aromatic and aliphatic ranges is defined by the peak height of the highest peak within each range's specific EICP in the highest standard used for range calibration. Print the EICP for each range in the highest calibration standard used after each initial calibration and record the highest peaks height count in y-axis units for each range.

10.5.11 After each initial calibration midpoint (25ug/mL) is reprocessed against the new curve, print the quant report and EICPs of the ranges where the peaks for COD and the IS are integrated separately using the C19-C36 range RFs, and 2-fluorobiphenyl, 2-bromonaphthalene, and OTP are integrated separately using the C11-C22 range RFs. Calculate the ratio of the apparent concentration using the range ions vs. the concentration on the quant report for the normal quant ions and enter this value in the N1 field of the method file for each surrogate and the IS. This factor will be used the quantitation of the ranges for samples as explained in Sec. 13.

10.6 GC/MS Sample Analysis

10.6.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with DFTPP tune verification and instrument calibration verification followed by sample extracts interspersed with blanks and QC samples. The sequence ends when the set of sample extracts has been injected or when more than 24 hours have elapsed since the DFTPP injection time. Mid-sequence calibration verification is not necessary due to the GC/MS use of internal standard calibration and detector stability. This modification is supported by the requirements of SW-846 GC/MS methods such as 8270 vs. the GC methods covered by method SW-846 Method 8000B. If requested by a customer ongoing calibration verification and terminal CCVs can be performed and reported. SIM analysis is performed using the same GC conditions and full scan EPH, however the MS method uses the special SIM ions and scan times for each analyte group. The groups are defined in Table 5.

10.6.2 Sample extracts and standards are introduced into the gas chromatograph by direct injection. Inject 2 µL of all standard, QC, and sample extracts using the HP7673 fast mode.

10.6.3 Confirm the retention time windows for each analyte of interest on a daily basis. Update the retention times whenever the target peaks drift significantly from the center or outside the windows established during initial calibration. Verify each target mass spectrum after updating and confirm that the range markers are properly placed. Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window.
Spectral confirmation occurs when the qualitative identity criteria below are met for each target analyte (excluding the ranges).

10.6.3.1 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 the HP 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.

10.6.3.2 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than

three such ions occur in the reference spectrum. (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%).

10.6.3.3 Isometric pairs should be resolved >90% to baseline except in the case of Benzo(b)fluoranthene and Benzo(k)fluoranthene. In this case, manual integration is performed by drawing parallel to the baseline and then stopping at the baseline point where the valley between the two isomers is deepest. This integration is performed on all calibration standards. Samples are integrated in the same way as the standards.

10.6.3.4 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component, i.e. a broadened peak with shoulder(s) or a valley between two or more maxima, appropriate selection of analyte spectra and background spectra is important.

10.6.3.5 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes co-elute (i.e. only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound. A good example of this is the co-elution of dimethyldihydroindene isomers and naphthalene under the GC conditions for EPH analysis. Careful examination of the EICPs and experimenting with spectral subtraction are necessary to separate the m/z 128 contribution from the target naphthalene and the non-target interferent.

10.6.4 Aliphatic and aromatic ranges of interest are determined by the collective integration of all peaks eluting between specified range "marker" compounds. Manual integration of the range EICPs is performed from baseline to baseline bounded by the tick marks of the range boundaries. Range boundaries are determined with each initial calibration and saved in the method file.

10.6.5 When quantifying on a peak area basis by internal calibration, collective peak area integration for the fractional ranges must be from baseline (i.e. must include the unresolved complex mixture "hump" areas). For the integration of individual Target Analytes, surrogate

compounds, and internal standards, a valley-to-valley approach should typically be used, though this approach may be modified on a case-by-case basis by an experienced analyst. Most single PAH or aliphatic analyte peaks should be resolved to baseline in the EICP of the quant ions. Quant ion selection is based on the SW-846 Method 8270C primary ion for the PAHs and the spectral base peak of the alkanes. Use valley-valley integration for closely eluting isomers and isomeric interferences.

10.6.6 If the Target or Diesel PAH Analytes are to be quantitated using this method, and the response for an individual analyte exceeds the calibration range of the system, dilute the extract and reanalyze. Report only data quantified within calibration range. The upper limit of calibration for the PAH analytes is based on the highest initial calibration standard level. Peak height is never used for target PAH quantitation.

10.6.7 For non-target analytes eluting in the aliphatic, aromatic or TPH fractions, the upper linear range of the system should be defined by peak height measurement, based upon the maximum peak height documented for an aliphatic or aromatic standard within the fraction that is shown to be within the linear range of the detector. Upper linear range for non-target peaks in the aromatic and aliphatic ranges is defined by the peak height of the highest peak within each range's specific EICP in the highest standard used for range calibration.

11.0 CALCULATIONS

11.1 Internal Standard calibration is employed. The hydrocarbon ranges are quantified using the summed response of the following characteristic ions:
C9-C18 Aliphatics: m/z 43, 57, 71, and 67
C19-C36 Alpihatics: m/z 43, 57, 72, and 67
C11-C22 Aromatics: m/z 50, 63, and 74

11.2 Aqueous samples:

The general equation to determine the concentration of a specific analyte or hydrocarbon range in aqueous samples is provided in Equation 6.

Equation 6

$$Concentration\ (ug/L) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(V_s)}$$

where:

A_x = Response of the analyte, hydrocarbon range/ TPH being measured, units may be in area counts or in peak height.

C_{is} = Amount of internal standard added to extract, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = Response of the internal standard, units same as A_x.

RF = Response factor for analyte or hydrocarbon range/TPH, dimensionless.

V_s = Volume of aqueous sample extracted, mL.

11.3 Non-aqueous samples:

The general equation to determine the concentration of a specific analyte or hydrocarbon range in soil or sediment samples is provided in Equation 7.

Equation 7

$$Concentration\ (ug/kg) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(W_d)}$$

where:

W_d = Dry weight of sample extracted, g. (See Equations 15 through 17)

A_x, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

11.4 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample extracted (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.8. Using the data obtained from Section 9.1.8, W_d is calculated using Equations 15 through 17.

Equation 15

$$\%\ Moisture = \frac{g\ sample - g\ dry\ sample}{g\ sample} X\ 100$$

Equation 16

$$\%\ Dry\ Solids = (100) - (\%\ Moisture)$$

Equation 17

$$W_d\ (g) = (\%\ Dry\ Solids / 100)(g\ of\ extracted\ sample)$$

12.0 QUALITY CONTROL

General Requirements, Minimum Instrument QC, and Daily Method QC Demonstrations

12.1 At a minimum each preparatory batch must contain a method blank, laboratory control sample, sample duplicate, and a matrix spike sample. Each analytical batch or queue is not required to include all preparatory QC. Analytical batches are limited by the 24hours sequence maximum, and not by sample number.

12.2 A system solvent blank must be run after a sample suspected of being highly contaminated to determine if sample carryover has occurred.

12.3 The recommended sequence of analysis for each analytical batch is as follows:

1. DFTPP tuning standard
2. Initial Calibration standards or Calibration Verification standard
3. Method Blank
4. Laboratory Control Sample
5. Samples

6. Sample Duplicate (following associated sample)
7. Sample Matrix Spike (following associated sample)

Note the LCS and MS are not analyzed in SIM queues because the spike concentrations exceed the SIM calibration range. In SIM queues duplicates are analyzed only if SIM is required on the duplicate sample. If requested by a customer ongoing calibration verification and terminal CCVs can be performed and reported.

12.4 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 25%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) must be at least 0.99.

12.5 The linear range of the aliphatic and aromatic hydrocarbon fractions, and/or TPH fraction, should be established based upon peak height. A series of analyses of high-concentration Aliphatic and Aromatic Hydrocarbon Standards should be undertaken to establish the upper linear range of each component within the fractions of interest (< 25% RSD). The peak height associated with the highest concentration standard that is still within the linear range of response is then used to establish the upper limits of linearity for any individual non-target peak contained on a sample chromatogram within the range(s) of interest.

12.6 Calibration check standards (CCV) are analyzed at the beginning of every analytical sequence. Mid-sequence or terminal calibration verification is not necessary due to the GC/MS use of internal standard calibration and detector stability. This practice is supported by the requirements of all SW-846 GC/MS methods such as SW-846 Method 8270C. If requested by a customer ongoing calibration verification and terminal CCVs can be performed and reported.

12.7 Each sample, blank, LCS, MS, and DUP must be spiked with the surrogate spiking solution. Required surrogate recovery is 40% to 140%. Recoveries outside this range must be noted and discussed on the data report form.

12.8 Every 20 sample preparatory batch should include a matrix spike and sample duplicate, if sufficient client sample is provided. Matrix spike duplicates will only be included per client request. If insufficient sample volume is provided for matrix spiking, then include as LCS duplicate (LCSD) in the prep batch.

12.9 Samples should be selected for spiking and sample duplicate at random and rotated among clients and sites from batch to batch. In some cases, the client may specify which sample is to be used for MS/MSD and sample duplicate; if not, the laboratory shall pick a representative sample based on the following:

A. MS/MSD shall **NOT** be performed on Rinsate Blank or Field Blank. Watch for client sample IDs containing codes like FB, EB, RB, etc. that might indicate a field blank sample.

B. Adequate sample weight/volume.

C. Client requested QC deliverables.

12.10 The instrument must be able to achieve adequate separation and resolution of peaks and analytes of interest.

12.10.1 The n-nonane (n-C_9) peak must be adequately resolved from the solvent front of the chromatographic run.

12.10.2 Surrogate peaks and internal standards may coelute with target analytes if the quantitation ion EICPs do not interfer.

12.10.3 All peaks of interest from the Aliphatic Hydrocarbon standard must be adequately resolved to baseline. In the Aromatic Hydrocarbon standard, baseline separation is expected for Phenanthrene and Anthracene. Benzo(a)Anthracene, Chrysene, Benzo(b)Fluoranthene, Benzo(k)flouranthene, Dibenzo(a,h)Anthracene, and Indeno(1,2,3-cd)Pyrene may not be chromatographically separated to baseline; however, sufficient separation should be obtained to 50% baseline.

12.11 Retention time windows must be established for each analyte of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 10.6.3)

12.12 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 25%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) must be at least 0.99. (See Section 9.4)

12.13 The linear range of the aliphatic and aromatic hydrocarbon fractions, and/or TPH fraction, should be established based upon peak height. The peak height associated with the highest concentration standard that is still within the linear range of response is then used to establish the upper limits of linearity for any individual non-target peak contained on a sample chromatogram within the range(s) of interest.

12.14 In order to demonstrate the absence of mass discrimination, the response ratio of C_{28} to C_{20} should be at least 0.85.

Initial and Periodic Method QC Demonstrations

The procedures specified in Section 12.15 through 12.17 must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

12.15 Accuracy and Precision:

To demonstrate initial laboratory capability, analyze a minimum of four replicate reagent water and/or clean sand blanks spiked with each analyte of interest at approximately 50 µg/L and/or 5 mg/kg, respectively.

12.15.1 Extract and analyze each replicate according to the procedures described in Section 9.0.

12.15.2 Calculate the measured concentrations of each analyte in all replicates, the mean accuracy (as a percentage of true value) for each analyte, and the precision (as %RSD) of the measurements for each analyte.

12.15.3 For each analyte, excluding n-C_{36}, the mean accuracy, expressed as a percentage of the true value, must be between 40% and 140%. Poorer recoveries may be experienced for the n-C_{36} standard. For each analyte, the %RSD must be less than or equal to 25%.

12.15.4 If desired, the Accuracy and Precision evaluation may be combined with the MDL evaluation specified in Paragraph 12.16.

12.16 Method Detection Limits for Individual Analytes:

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with all analytes of interest at the default reporting limits for each matrix. MDL spiking concentrations for single analytes should result in extract solution concentrations equivalent to the lowest calibration standard. Typical spiking concentrations for analytes of interest are 1 µg/L for water, and 0.25 mg/kg for soil. Extract and analyze each replicate according to the procedures described in Section 9.0. Calculate the Method Detection Limit (MDL), Minimum Level (ML) and Reporting Limit (RL) of each analyte using the procedures described in Section 12.0.

12.16.1 Water MDLs are determined by extracting 7 to 10 replicates of 1-L reagent water blanks spiked with OTP, COD and each analyte of interest.

12.16.2 Soil/sediment MDLs are determined by extracting 7-10 replicates of 20-g of EPH-free sand blanks spiked with OTP, COD, and each analyte of interest.

12.16.3 For each analyte, excluding n-C_{36}, the mean accuracy, expressed as a percentage of the true value, must be between 40% and 140%. Poorer recoveries may be experienced for the n-C_{36} standard. For each analyte, the %RSD must be less than or equal to 25%.

12.17 Method Detection Limits for Hydrocarbon Ranges:

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with diesel fuel at a concentration near or below the MCP regulatory level for the most toxic hydrocarbon range, e.g. the aromatic C11-C22 range. Typical total diesel fuel spiking concentrations are 0.25 mg/L for water, and 125 mg/kg for soil. Extract and analyze each replicate according to the procedures described in Section 9.0. Calculate the Method Detection Limit (MDL), Minimum Level (ML) and Reporting Limit (RL) of each hydrocarbon range using the procedures described in Section 12.0.

12.17.1 Water MDLs are determined by extracting 7 to 10 replicates of 1-L reagent water blanks spiked with OTP, COD and the petroleum reference standard. Prepare a petroleum reference standard spiking solution by diluting the petroleum reference stock standard solution with acetone to a concentration of approximately 2500ug/mL. Spike a 1-Liter reagent water blank

with 0.100 mL of this spiking solution. MDL spiking concentrations for the hydrocarbon ranges in water should be no more than 125ug/L each for the aromatic and aliphatic ranges.

12.17.2 Soil/sediment MDLs are determined by extracting 7-10 replicates of 20-g sand blanks spiked with OTP, COD, and the petroleum reference standard. Prepare a petroleum reference standard spiking solution by diluting the petroleum reference stock standard solution with acetone to a concentration of approximately 2500ug/mL. Spike 20 g of clean sand blanks with 1.0 mL of this spiking solution. MDL spiking concentrations for the hydrocarbon ranges in soil should be no more than 62.50 ug/g each for the aromatic and aliphatic ranges. Using the API/EPA high aromatic fuel oil#2 spike at 125 ug/g will meet this criteria.

12.17.3 The mean recovery of the summation of all (unadjusted) hydrocarbon ranges (i.e., including Target Analytes), expressed as a percentage of the true value of the petroleum reference standard, must be between 40% and 140%. For each hydrocarbon range, the %RSD must be less than or equal to 25%.

13.0 DATA PRODUCTION AND REPORTING

13.1 Calibration:

Using the internal calibration procedure, calibrate the GC as follows:

13.1.1 Calculate an RRF, or LR for the individual PAH compounds, aliphatic hydrocarbons, and surrogates that comprise the calibration standard.

13.1.2 Calculate a collective RRF, or LR for the total mass concentration of the C_9 -C_{18} Aliphatic Hydrocarbons. Tabulate the summation of the peak areas of all component standards in that fraction (e.g., C_9-C_{18} Aliphatics, 6 components) against the total on column mass injected.

13.1.3 Calculate a collective RRF, or LR for the total mass concentration of the C_{19} -C_{36} Aliphatic Hydrocarbons. Tabulate the summation of the peak areas of all component standards in that fraction (e.g., C_{19}-C_{36} Aliphatics, 10 components) against the total mass injected. The contribution of COD and the IS is included in the C19-C36 Aliphatic range during calibration, both in the integration and concentration

calculation. This makes data processing easier and does not adversely affect the RF. Determine the ratio of the aliphatic range m/z set response of COD and the IS to their single analyte quant-ion response and include this factor in the N1 field of the method file for surrogate and internal standard contribution correction when quantifying samples.

13.1.4 Calculate a collective RRF or LR for the total mass concentration of the C_{11} -C_{22} Aromatic Hydrocarbons. Tabulate the summation of the peak areas of all component standards in that fraction (e.g., C_{11}-C_{22} Aromatics, 20 components) against the total mass injected. The contributions of OTP, 2-Bromonaphthalene (2BRN), and 2-Fluorobiphenyl (2FB) are included in the C11-C22 Aromatic range during calibration, both in the integration and concentration calculation. Determine the ratio of the aromatic range m/z set response of OTP, 2BRN, and 2FB separately and enter the factor in the N1 fields for each compound in the method file for surrogate contribution correction when quantifying samples.

13.2 Sample Analysis

13.2.1 Aliphatic Fractions:

13.2.1.1 Determine the total EICP area (sum of m/z 43, 57, 71, and 67) for all peaks eluting between 0.1 min before n-C9 and 0.01 min before the beginning of the upslope of the n-C19 peak.

13.2.1.2 Determine the total EICP area (sum of m/z 43, 57, 71, and 67) for all the peaks eluting between 0.01 min before the beginning of the up slope of the nC-19 peak and 0.1 min after the tail of the n-C36 peak.

13.2.1.3 Determine the concentration of COD and the IS, adjust them by the respective range ions / quant ion response ratio, and then subtract this concentration sum from the C19-C36 Aliphatic Range concentration. The macro CALCMUL2 automatically performs this calculation from the COD and IS concentrations and the ratios stored in the N1 user defined field in the EPHX.m quantitation method. The report to screen function generates the LIMS import file with the adjusted and unadjusted ranges. The adjusted ranges are used for LIMS report calculations.

13.2.2 Aromatic Fraction:

13.2.2.1 Determine the total EICP area (m/z 50, 63, and 74) for all peaks eluting between 0.1 min before RT of naphthalene and 0.1 min after the RT of benzo(g,h,i)perylene.

13.2.2.2 Determine the concentrations of OTP, 2BRN, and 2FB, and adjust them by the respective range ions/quant ion response ratio, add the sum of all the PAH target analyte concentrations, and subtract this new sum from the C11-C22 Aromatic Range concentration to produce the final adjusted C11-C22 Aromatic Range concentration. The macro CALCMUL2 automatically performs this calculation from the OTP, 2BRN, and 2FB concentrations and the ratios stored in the N1 user defined field in the EPHX.m quantitation method. (Note: the PAH target analyte concentrations are not adjusted by the range ion/ quant ion response ratios before subtraction, which allows the data user to calculate the Unadjusted C11-C22 Aromatic Range concentration by adding the PAH concentrations to the adjusted C11-C22 Aromatic Range result.)

13.2.2.3 Determine the peak area count for the Target or Diesel PAH Analytes.

13.2.2.4 The print to screen function for the Generate Report function on SV-1 and SV-2 has been modified to calculate the raw (no adjustment for surrogates or PAHs) and adjusted (corrected for both surrogate and PAH contributions) range values for import to the LIMS. The Unadjusted C11-C22 value (adjusted for the surrogates but not the PAHs) is not calculated or reported to the client unless specifically requested.

13.2.2.5 The laboratory reports the adjusted aromatic range value and always quantifies the PAHs even if they are not reported to the client.

13.2.3 Data Manipulations:

13.2.3.1 By definition, the collective concentration of the aromatic fraction (and/or TPH) **excludes** the individual concentrations of the Target PAH Analytes. Accordingly, a data manipulation step is necessary to adjust the collective range concentration calculated in 13.2.2.2 and 13.2.2.4, to eliminate "double counting" of analytes.

13.2.3.2 The adjusted aromatic and aliphatic range values and always quantifies the PAHs even if they are not reported to the client. All manipulations are performed by the macro programs to avoid transcription errors. The CALCMUL2 macro calculates the reportable results in soil of water units for all EPH target analytes, both single analyte and adjusted range results, from the on-column results in the quant.res file where the multiplier is 1. The correct multiplier is calculated from the dilution factor (DF=x) in the 'Samp' field after the bracketed sample ID, and in the 'Misc.' field the extract final volume (FV=x), sample amount (SAMP=xx.xxG or xxxxML), and %solids if applicable (S=xx.x) using the formulas defined in Eq.12-14 above. Only the correctly adjusted C19-C36 Aliphatics and C11-C22 Aromatics (see the 13.2.1.3 and 13.2.2-5 section modifications above) are reported to the client. The CALCMUL2 output is labeled Macro Modified Quantitation Report at the top. The LIMS Quantitation Report data is imported to and used by the LIMS to calculate the client deliverable report, therefore the CALCMUL2 report is independent and can be used to verify the correct format, prep data, and %solids data have been used.

13.2.3.3 The adjusted aromatic range value and always quantifies the PAHs even if they are not reported to the client.

13.2.3.4 For purposes of compliance with the reporting and cleanup standards specified in the Massachusetts Contingency Plan, the concentration of Unadjusted C_{11} through C_{22} Aromatic Hydrocarbons and/or Unadjusted TPH may be conservatively deemed to be equivalent to the concentration of C_{11} through C_{22} Aromatic Hydrocarbons and/or TPH

13.2.4 Data Reporting Format:

13.2.4.1 The data elements in the required data reporting format (Appx. 3 of the MA DEP EPH method) are produced in AMRO's default EPH LIMS report format (see Attachment 4).

13.2.4.2 The significant modifications of the MA DEP method are summarized in Attachment 3 and include the following:

13.2.4.2.1 Silica-gel cleanup is not performed. Separation of the aromatic and aliphatic hydrocarbons is accomplished using a mass spectrometer.

13.2.4.2.2 A mass spectrometer is used in lieu of the FID detector.

13.2.5 Reporting Limits:

The Reporting Limits (RLs) for individual analytes and hydrocarbon ranges shall be experimentally determined by each laboratory using this method. Although laboratories have flexibility in performing this task, in order to ensure the validity and meaningfulness of these concentration values, the following performance standards must always be achieved:

- The RLs for individual analytes must be established by the analyses of at least 7 replicate water and/or sand blanks fortified with the individual analytes of interest;
- The RLs for the hydrocarbon ranges must be established by the analyses of at least 7 replicate water and/or sand blanks fortified with a petroleum reference standard;
- The RL for individual analytes may be set no higher than the lowest calibration standard which is still within the linear range of the calibration curve (i.e, less than 25% RSD), assuming 100% extraction of the sample matrix; and
- The RL for individual analytes must be verified by the analyses of at least 4 replicate water or sand blanks fortified at the Reporting Limit, where the precision of replicate analyses is demonstrated to be equal to or less than 25% RSD, and the mean accuracy is demonstrated to be between 40-140% of the spiked value.

13.3 Individual Analytes

The Reporting Limit (RL) for individual analytes of interest should be calculated by first determining a Method Detection Limit (MDL) for each analyte, and then applying an adjustment factor to the MDL to calculate the Minimum Level (ML).

13.3.1 The MDL is determined by the analysis of 7-10 replicate samples, as detailed in Section 10.3.2. The data obtained from these analyses are then use to calculate the MDL using Equation 18.

Equation 18

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level.
SD = standard deviation of the replicate analysis.

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

13.3.2 The Minimum Level (ML) is then calculated from the MDL according to equation 19:

Equation 19

$$ML = (MDL) \times (3.18)$$

13.3.3 If the ML is greater than the concentration of analyte used in the MDL study, the Reporting Limit is this value. If the ML is less than the concentration of analyte used in the MDL study, the laboratory may either (a) establish the RL at the concentration of the analyte used in the MDL study, or (b) undertake additional analyses to demonstrate method performance at the ML.

13.3.3.1 To demonstrate adequate method performance at the calculated ML and proposed RL, analyze at least 4 replicate water and/or sand samples fortified with the analytes of interest at the ML.

13.3.3.2 The mean recovery of each analyte, expressed as a percentage of the true value, must be between 40-140%. For each analyte, the %RSD of replicate analyses must be less than or equal to 25%.

13.3.3.3 If necessary, a low-level calibration standard must be prepared at the concentration of the proposed RL, assuming 100% extraction from the sample matrix. This standard must be analyzed and shown to be within the linear range of the calibration curve (i.e., %RSD equal to or less than 25%). Note that the recommended analyte concentrations for the MDL studies specified in Section 13.3.2 are equivalent to the lowest calibration standard recommended in Table 5, assuming 100% extraction from the sample, and the recommended sample preparation and analysis procedures specified in this method.

13.4 Collective Hydrocarbon Ranges/TPH

The Reporting Limit (RL) for each hydrocarbon range, and/or for TPH should be calculated by first determining a Method Detection Limit (MDL) for each range and/or for TPH, and then applying an adjustment factor to the MDL to calculate the Minimum Level (ML).

13.4.1 The MDL is determined by the analysis of 7-10 replicate samples, as detailed in Section 10.3.3. The data obtained from these analyses are then use to calculate the MDL using Equation 18.

13.4.2 The Minimum Level (ML) is then calculated from the MDL according to equation 19.

13.4.3 If the ML is greater than the mean concentration of the hydrocarbon range determined in the MDL study, the Reporting Limit is this value. If the ML is less than the mean concentration of the hydrocarbon range determined in the MDL study, the laboratory may either (a) establish the RL at the concentration of the hydrocarbon range determined in the MDL study, or (b) undertake additional analyses to demonstrate method performance at the ML. AMRO default reporting limits are based on the initial MDL study using the EPA/API fuel oil #2 reference material.

13.4.3.1 To demonstrate adequate method performance at the calculated ML and proposed RL, analyze at least 4 replicate water and/or sand samples fortified with the petroleum reference standard at or near the range MLs of interest. For range MLs, this will involve assumptions on the chemistry of the petroleum reference standard, based upon data obtained during the MDL studies. **AMRO** uses the neat EPA/API high aromatic fuel oil #2 reference material (WP 681) available from RTC (#954-020). This fuel is characterized with respect to total aromatic and total aliphatic hydrocarbon content so the assumptions are reduced to a minimum.

13.4.3.2 The mean recovery of the summation of each range, and/or TPH, expressed as a percentage of the true value of the petroleum reference standard, must be between 40-140%. For each range and/or TPH, the %RSD of replicate analyses must be less than or equal to 25%.

Attachment 1

AMRO Environmental
Laboratories Corporation

111 Herrick Street
Merrimack, NH 03054
(603) 424-2022

QUALIFICATION CARD FOR METHOD MADEP-EPH

Trainee: _____ Signature: _____

Trainer: _____ Signature: _____

I. Knowledge Factors:

SOP Title: _____ Revision Number/Date: _____

1. Did the Trainee read and understand the above SOP?	Yes ☐	No ☐	NA ☐
2. Was the Trainee instructed on how to properly fill out the documentation?	Yes ☐	No ☐	NA ☐
3. Has the Trainee been instructed on the proper procedures for addressing potential problems?	Yes ☐	No ☐	NA ☐

II. Practical Factors:

1. Has the Trainee completed a Precision and Accuracy Study?	Yes ☐	No ☐	NA ☐
2. Has the Trainee completed an acceptable Performance Evaluation sample?	Yes ☐	No ☐	NA ☐
3. Did the Trainee completed an acceptable Laboratory Control Sample (LCS)?	Yes ☐	No ☐	NA ☐
4. Has the Trainee performed manual integration as indicated in the SOP?	Yes ☐	No ☐	NA ☐

Completion Date: _____ Trainer's Signature: _____

I _____ have read, understood and follow the above method/SOP, which is in use at AMRO Laboratories for the analysis of samples under the National Environmental Laboratory Accreditation Program, have met the Demonstration of Capability.

Section Manager/ Supervisor: _____ Date: _____

QA Manager: _____ Date: _____

qc/qcmemos/forms/EPHqualcard Rev. 0 01/01

Attachment 2

AMRO Environmental
Laboratories Corporation

111 Herrick Street
Merrimack, NH 03054
(603) 424-2022

GC AND GC/MS DATA REVIEW CHECKLIST

LAB ORDER: _____ **CLIENT:** _____

Method:	**Sample(s) No.:**
Analysis:	**Matrix:**

A.	**GENERAL**			
1.	Copy of Prep/Extraction Log?	Y	N	NA
2.	Copy of Instrument Run Log or Tune List?	Y	N	NA
3.	Copy of dry weight log present?	Y	N	NA
4.	Are all sample checked for preservation after VOA analysis?	Y	N	NA
5.	All samples met extraction and/or analysis holding time criteria?	Y	N	NA
6.	Did the Tune pass and DFTPP or BFB injected every 12 hours?	Y	N	NA
7.	Are the surrogate recoveries for each sample within the QC limits?	Y	N	NA
8.	Method Blank- contaminant free?	Y	N	NA
9.	Initial Calibration meets method criteria for all compounds reported?	Y	N	NA
10.	Continuing Calibration meets method criteria for all compounds reported?	Y	N	NA
11.	Are all reported results within calibration range?	Y	N	NA
12.	LCS % Recovery criteria met for all compounds?	Y	N	NA
13.	MS/MSD %R's and %RPD's are met for all compounds?	Y	N	NA
14.	%RPD criteria met between sample and duplicate?	Y	N	NA
15.	Samples checked for carry over from sample to sample due to target or nontarget overload?	Y	N	NA
16.	Are all data exported to LIMS, calculated and verified?	Y	N	NA

COMMENTS

Analyst (s) _____ DATE: _____

REVIEWER: _____ DATE OF REVIEW: _____

qc/qcmemos/Forms/gcmschecklist Rev. 1 04/00

Attachment 4

AMRO Environmental Laboratories Corp.

Date: *05-Apr-01*

CLIENT: Client Sample ID:
Lab Order: Tag Number:
Project: Collection Date:
Lab ID: Matrix:

Analyses	Result	RL	Qual	Units	DF	Date Analyzed
EXTRACTABLE PETROLEUM HYDROCARBONS MAEPH						Analyst: GG
C9-C18 Aliphatic Hydrocarbons	ND	100		µg/L	1	3/29/01 2:25:00 AM
C19-C36 Aliphatic Hydrocarbons	ND	100		µg/L	1	3/29/01 2:25:00 AM
C11-C22 Aromatic Hydrocarbons	ND	100		µg/L	1	3/29/01 2:25:00 AM
Naphthalene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
2-Methylnaphthalene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Acenaphthylene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Acenaphthene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Fluorene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Phenanthrene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Anthracene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Fluoranthene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Pyrene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Benz(a)anthracene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Chrysene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Benzo(b)fluoranthene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Benzo(k)fluoranthene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Benzo(a)pyrene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Dibenz(a,h)anthracene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Indeno(1,2,3-cd)pyrene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Benzo(g,h,i)perylene	ND	1.0		µg/L	1	3/29/01 2:25:00 AM
Surr: 1-Chlorooctadecane	84.6	40-140		%REC	1	3/29/01 2:25:00 AM
Surr: 2-Bromonaphthalene	117	40-140		%REC	1	3/29/01 2:25:00 AM
Surr: 2-Fluorobiphenyl	119	40-140		%REC	1	3/29/01 2:25:00 AM
Surr: o-Terphenyl	83.8	40-140		%REC	1	3/29/01 2:25:00 AM

Hydrocarbon range data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range. EPH: C11-C22 Aromatic Hydrocarbons exclude the concentration of target PAH analytes. VPH: C5-C8 Aliphatic Hydrocarbons exclude the concentration of target analytes eluting in this range. C9-C12 Aliphatic Hydrocarbons exclude the concentration of target analytes eluting in this range and concentration of C9-C10 Aromatic Hydrocarbons.

CERTIFICATION

Were all QA/QC procedures required by the VPH or EPH method followed: ___ Yes ___ No - If No, See Case Narrative

Were all performance/acceptance standards for required QA/QC procedures achieved: ___ Yes ___ No - If No, See Case Narrative

Were any significant modifications made to the method as specified in section 11.3: ___ No ___ Yes - Details enclosed

I attest under the pains and penalties of perjury that, based upon my inquiry of those individuals immediately responsible for obtaining the information, the material contained in this report is, to the best of my knowledge and belief, accurate and complete.

SIGNATURE. _____ DATE: _____

PRINTED NAME. Nancy Stewart POSITION: Laboratory Director (or designee)

Qualifiers: RL - Reporting Limit, defined as the lowest concentration the laboratory can accurately quantitate.

ND - Not Detected at the Reporting Limit S - Spike Recovery outside accepted recovery limits E - Value above quantitation range

J - Analyte detected below quantitation limits R - RPD outside accepted recovery limits # - See Case Narrative

B - Analyte detected in the associated Method Blank H - Method prescribed holding time exceeded

Compound	Reporting Limit	Spike level ug/L	% Recovery	Mean ug/L	Std Dev	MDL	DL<Spike?	0204.d	0205.d	0206.d	0208.d	0209.d	0210.d	0211.d
1,2-Dibromoethane	1	1.0	83.6	0.84	0.06	0.19	yes	0.869	0.784	0.780	0.875	0.889	0.901	0.752
2-Chloroethyl-Vinyl-ether	5	5.0	91.1	4.55	0.54	1.70	yes	5.220	5.190	4.120	4.870	4.470	4.070	3.940
2-Hexanone	5	1.0	87.6	0.88	0.19	0.60	yes	0.871	1.083	0.625	0.858	0.899	1.129	0.662
1,3-Dichloropropane	1	1.0	89.4	0.89	0.03	0.10	yes	0.861	0.873	0.892	0.961	0.885	0.891	0.894
Tetrachloroethene	1	1.0	67.3	0.67	0.07	0.23	yes	0.778	0.573	0.628	0.657	0.759	0.630	0.688
Dibromochloromethane	1	1.0	85.4	0.85	0.07	0.23	yes	0.744	0.843	0.914	0.879	0.949	0.872	0.778
Chlorobenzene	1	1.0	82.2	0.82	0.06	0.19	yes	0.903	0.768	0.847	0.897	0.789	0.763	0.788
1,1,1,2-Tetrachloroethane	1	1.0	96.8	0.97	0.16	0.51	yes	0.783	0.747	1.086	1.079	0.876	1.148	1.055
Ethylbenzene	1	1.0	82.2	0.82	0.04	0.12	yes	0.886	0.786	0.808	0.831	0.827	0.843	0.770
m,p-Xylene	1	2.0	80.1	1.60	0.07	0.24	yes	1.575	1.643	1.498	1.687	1.681	1.519	1.608
o-Xylene	1	1.0	77.9	0.78	0.06	0.20	yes	0.755	0.701	0.740	0.818	0.858	0.727	0.852
Styrene	1	1.0	82.7	0.83	0.04	0.13	yes	0.871	0.811	0.847	0.870	0.788	0.838	0.762
Bromoform	1	1.0	81.4	0.81	0.04	0.12	yes	0.766	0.869	0.809	0.851	0.792	0.835	0.775
Isopropylbenzene	1	1.0	72.1	0.72	0.04	0.14	yes	0.784	0.684	0.719	0.758	0.724	0.648	0.732
Cyclohexanone	100	10.0	268.3	26.83	1.06	3.33	yes	27.199	26.121	28.255	27.877	26.758	25.144	26.461
1,1,2,2-Tetrachloroethane	1	1.0	88.8	0.89	0.06	0.18	yes	0.849	0.852	0.911	0.952	0.970	0.815	0.869
1,2,3-Trichloropropane	1	1.0	119.5	1.19	0.10	0.31	yes	1.050	1.198	1.124	1.366	1.176	1.244	1.204
Bromobenzene	1	1.0	74.9	0.75	0.07	0.23	yes	0.764	0.685	0.828	0.862	0.710	0.672	0.722
n-Propylbenzene	1	1.0	76.7	0.77	0.04	0.14	yes	0.806	0.738	0.765	0.832	0.708	0.786	0.736
2-Chlorotoluene	1	1.0	81.8	0.82	0.03	0.09	yes	0.837	0.859	0.812	0.839	0.812	0.788	0.776
4-Chlorotoluene	1	1.0	80.2	0.80	0.04	0.12	yes	0.812	0.816	0.764	0.863	0.784	0.750	0.825
1,3,5-Trimethylbenzene	1	1.0	72.3	0.72	0.04	0.12	yes	0.719	0.684	0.741	0.705	0.716	0.696	0.803
tert-Butylbenzene	1	1.0	70.3	0.70	0.03	0.10	yes	0.715	0.673	0.711	0.676	0.747	0.669	0.731
1,2,4-Trimethylbenzene	1	1.0	80.0	0.80	0.04	0.12	yes	0.738	0.804	0.794	0.859	0.805	0.778	0.824
sec-Butylbenzene	1	1.0	70.0	0.70	0.06	0.19	yes	0.769	0.662	0.652	0.743	0.705	0.610	0.762
4-Isopropyltoluene	1	1.0	73.3	0.73	0.04	0.12	yes	0.806	0.682	0.723	0.747	0.727	0.710	0.738
1,3-Dichlorobenzene	1	1.0	81.9	0.82	0.03	0.11	yes	0.796	0.866	0.786	0.820	0.863	0.782	0.821
1,4-Dichlorobenzene	1	1.0	78.6	0.79	0.07	0.22	yes	0.884	0.725	0.837	0.832	0.683	0.742	0.801
n-Butylbenzene	1	1.0	81.2	0.81	0.04	0.14	yes	0.899	0.799	0.818	0.812	0.816	0.790	0.751
1,2-Dichlorobenzene	1	1.0	87.1	0.87	0.05	0.16	yes	0.900	0.831	0.900	0.784	0.914	0.853	0.917
1,2-Dibromo-3-chloropropane	2	2.0	124.7	2.49	0.44	1.40	yes	2.610	1.900	2.840	2.630	2.860	2.800	1.820
1,2,3-Trichlorobenzene	1	1.0	73.5	0.73	0.23	0.71	yes	0.394	0.886	0.956	0.437	0.849	0.775	0.847
Hexachlorobutadiene	1	1.0	113.6	1.14	0.10	0.31	yes	1.116	1.102	1.261	1.153	1.138	1.228	0.952
Naphthalene	2	1.0	156.6	1.57	0.21	0.65	yes	1.570	1.553	1.504	2.006	1.539	1.395	1.393
1,2,4-Trichlorobenzene	1	1.0	116.7	1.17	0.13	0.40	yes	1.378	1.093	1.126	1.228	1.216	0.963	1.163

20-Feb-02						10ppb-->	e9909.D	e9910.D	e9911.D	e9912.D	e9913.D	e9914.D	e9915.D
8260 low soil v-2 sk						5ppb-->	e9929.D	e9924.D	e9925.D	e9926.D	e9927.D	e9928.D	e9922.D
Compound	Spike level	Mean	% Rec	Std Dev	MDL	MDL < Spike?							
	ug/kg	ug/kg				Yes or No?	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg
Dichlorodifluoromethane	5	2.75	54.93	0.30	0.93	YES	2.22	2.93	2.87	2.82	2.94	2.44	3.00
Chloromethane	5	4.69	93.72	0.23	0.74	YES	4.30	4.66	4.71	4.85	4.72	4.52	5.04
Vinyl Chloride	5	4.60	91.93	0.46	1.45	YES	4.01	4.85	4.48	4.76	4.39	4.26	5.42
Chloroethane	5	4.79	95.77	0.46	1.46	YES	4.51	5.01	4.42	4.63	4.65	4.55	5.75
Bromomethane	5	5.07	101.34	0.58	1.83	YES	4.50	5.18	4.39	4.67	5.13	5.72	5.88
Dichloroflouromethane	5	4.71	94.26	0.41	1.28	YES	4.30	5.33	4.36	4.59	4.48	4.71	5.22
Trichlorofluoromethane	5	4.30	86.09	0.55	1.72	YES	3.62	4.24	4.00	4.31	4.37	4.18	5.41
Diethyl Ether	5	4.96	99.25	0.36	1.13	YES	4.55	4.86	5.25	5.20	4.64	5.51	4.74
Acetone	10	7.16	71.63	1.26	3.97	YES	7.10	6.94	6.30	6.37	9.71	7.72	6.00
1,1-Dichloroethene	5	5.05	100.94	0.66	2.06	YES	4.17	5.66	4.90	4.98	4.70	4.77	6.15
Carbon Disulfide	5	4.83	96.57	0.64	2.02	YES	4.25	4.90	4.69	4.72	4.65	4.39	6.20
Methylene Chloride	10	14.60	146.03	1.29	4.04	YES	15.65	15.16	14.25	16.05	14.96	13.94	12.21
Methyl tert-butyl ether	5	5.22	104.39	0.27	0.85	YES	4.83	5.28	5.04	5.33	5.21	5.15	5.70
trans-1,2-Dichloroethene	5	5.02	100.39	0.55	1.73	YES	4.87	5.26	4.77	4.61	4.81	4.65	6.17
Tertiary Butanol	100	73.39	73.39	7.33	23.03	YES	67.19	72.63	65.19	80.25	85.67	73.65	69.14
1,1-Dichloroethane	5	4.86	97.16	0.43	1.36	YES	4.30	5.10	4.77	4.83	4.84	4.51	5.65
Diisopropyl ether	5	5.28	105.53	0.29	0.91	YES	4.87	5.37	5.20	5.30	5.12	5.26	5.82
Ethyl tertiary butyl ether	5	5.82	116.48	0.42	1.32	YES	5.09	6.00	5.81	5.84	5.92	5.62	6.48
2-Butanone	10	8.04	80.37	1.20	3.77	YES	5.50	7.94	7.89	8.31	8.93	8.90	8.79
2,2-Dichloropropane	5	5.39	107.72	0.66	2.08	YES	4.77	6.00	5.44	5.14	4.90	4.91	6.54
cis-1,2-Dichloroethene	5	5.08	101.58	0.40	1.27	YES	4.72	4.97	5.09	4.91	4.93	4.97	5.96
Chloroform	5	5.09	101.85	0.45	1.40	YES	4.81	5.13	5.04	4.92	4.93	4.75	6.06
Tetrahydrofuran	10	6.63	66.27	0.73	2.30	YES	6.03	6.69	7.64	7.00	6.86	6.81	5.36
Bromochloromethane	5	5.20	103.97	0.23	0.74	YES	5.31	5.35	5.08	4.78	5.12	5.25	5.50
1,1,1-Trichloroethane	5	4.61	92.21	0.38	1.18	YES	4.23	4.56	4.56	4.44	4.55	4.52	5.42
1,1-Dichloropropene	5	5.12	102.49	0.42	1.31	YES	4.68	5.08	5.25	4.92	4.92	5.04	5.98
Carbon Tetrachloride	5	4.10	82.06	0.44	1.38	YES	3.58	4.08	3.95	4.18	3.91	4.02	5.00
1,2-Dichloroethane	5	4.79	95.72	0.22	0.68	YES	5.05	4.66	4.42	4.67	4.93	4.87	4.91
Benzene	5	5.08	101.62	0.30	0.93	YES	4.89	4.97	4.89	5.02	5.01	5.05	5.74
Tertiary amyl methyl ether	5	5.53	110.64	0.15	0.46	YES	5.37	5.48	5.51	5.56	5.79	5.63	5.38
Trichloroethene	5	4.64	92.74	0.26	0.81	YES	4.20	4.82	4.63	4.81	4.46	4.57	4.97
1,2-Dichloropropane	5	4.70	94.05	0.31	0.97	YES	4.44	5.05	4.87	4.72	4.25	4.53	5.05
Bromodichloromethane	5	4.08	81.60	0.22	0.68	YES	3.72	4.25	4.17	4.13	3.94	3.99	4.37
Dibromomethane	5	4.71	94.25	0.20	0.64	YES	4.43	4.47	4.71	4.76	4.74	4.91	4.97
4-Methyl-2-pentanone	10	8.73	87.26	0.38	1.18	YES	8.27	8.66	8.76	8.50	8.94	9.43	8.52
cis-1,3-Dichloropropene	5	4.21	84.17	0.32	0.99	YES	3.80	4.32	4.39	4.09	4.08	4.01	4.77
Toluene	5	4.95	99.03	0.25	0.79	YES	4.68	4.87	5.14	4.73	4.89	4.94	5.41
trans-1,3-Dichloropropene	5	4.92	98.49	0.23	0.74	YES	4.62	5.13	4.73	4.92	4.97	4.81	5.30
1,1,2-Trichloroethane	5	4.76	95.22	0.20	0.63	YES	4.57	4.56	4.75	4.95	4.59	4.84	5.07
1,2-Dibromoethane	5	4.71	94.18	0.12	0.38	YES	4.67	4.70	4.66	4.69	4.76	4.54	4.94
2-Hexanone	10	6.60	66.01	0.16	0.49	YES	6.45	6.87	6.70	6.70	6.52	6.48	6.49
1,3-Dichloropropane	5	4.99	99.75	0.18	0.56	YES	4.98	4.82	5.15	5.08	5.07	5.13	4.67
Tetrachloroethene	5	4.37	87.32	0.21	0.67	YES	4.40	4.27	4.25	4.25	4.12	4.50	4.77
Dibromochloromethane	5	4.69	93.87	0.07	0.22	YES	4.63	4.72	4.75	4.68	4.81	4.60	4.66
Chlorobenzene	5	4.96	99.29	0.14	0.43	YES	4.76	5.13	4.88	4.86	5.11	4.98	5.03
1,1,1,2-Tetrachloroethane	5	4.11	82.26	0.17	0.53	YES	4.12	4.00	4.06	4.29	4.06	3.89	4.37
Ethylbenzene	5	4.72	94.50	0.10	0.32	YES	4.78	4.81	4.65	4.66	4.56	4.83	4.78

m,p-Xylene	10	9.59	95.92	0.36	1.14	YES	9.78	9.30	9.23	9.38	9.36	10.14	9.96
o-Xylene	5	4.77	95.44	0.14	0.44	YES	4.74	4.80	4.60	4.77	4.70	5.05	4.74
Styrene	5	4.72	94.50	0.10	0.31	YES	4.66	4.88	4.56	4.70	4.74	4.75	4.78
Bromoform	5	5.15	103.02	0.57	1.79	YES	5.30	5.45	5.44	5.37	3.87	5.34	5.29
Isopropylbenzene	5	4.46	89.30	0.28	0.88	YES	4.79	4.58	4.16	4.30	4.21	4.36	4.86
1,1,2,2-Tetrachloroethane	5	4.54	90.72	0.18	0.56	YES	4.48	4.63	4.70	4.79	4.38	4.48	4.29
1,2,3-Trichloropropane	5	4.66	93.13	0.26	0.81	YES	4.85	4.82	4.67	4.80	4.62	4.74	4.10
Bromobenzene	5	4.67	93.41	0.26	0.82	YES	4.40	4.92	4.37	4.95	4.72	4.45	4.89
n-Propylbenzene	5	4.42	88.37	0.28	0.87	YES	4.86	4.46	4.07	4.25	4.19	4.43	4.67
2-Chlorotoluene	5	4.85	97.05	0.23	0.71	YES	4.96	4.76	4.67	4.80	4.62	4.87	5.29
4-Chlorotoluene	5	4.76	95.13	0.19	0.60	YES	4.98	4.90	4.51	4.81	4.56	4.62	4.92
1,3,5-Trimethylbenzene	5	4.56	91.17	0.25	0.77	YES	4.98	4.63	4.36	4.61	4.19	4.55	4.59
tert-Butylbenzene	5	4.39	87.74	0.34	1.06	YES	4.98	4.55	3.96	4.30	4.07	4.39	4.46
1,2,4-Trimethylbenzene	5	4.64	92.75	0.28	0.88	YES	5.19	4.58	4.40	4.66	4.31	4.60	4.71
sec-Butylbenzene	5	4.16	83.14	0.28	0.87	YES	4.67	4.22	3.85	4.13	3.85	4.21	4.18
4-Isopropyltoluene	5	4.40	88.09	0.33	1.03	YES	5.00	4.36	4.04	4.46	4.03	4.55	4.38
1,3-Dichlorobenzene	5	4.79	95.87	0.27	0.86	YES	5.34	4.85	4.56	4.87	4.52	4.69	4.73
1,4-Dichlorobenzene	5	4.77	95.38	0.21	0.65	YES	5.19	4.70	4.66	4.72	4.52	4.82	4.77
n-Butylbenzene	5	4.16	83.12	0.27	0.84	YES	4.60	4.27	3.93	4.01	3.83	4.35	4.10
1,2-Dichlorobenzene	5	4.80	96.01	0.17	0.54	YES	5.06	4.72	4.69	4.87	4.54	4.95	4.77
1,2-Dibromo-3-chloropropane	5	5.70	113.97	0.28	0.89	YES	5.58	5.34	5.83	5.63	6.25	5.66	5.60
1,2,4-Trichlorobenzene	5	4.78	95.51	0.59	1.85	YES	5.92	4.65	4.47	4.74	4.60	5.03	4.02
Hexachlorobutadiene	5	3.87	77.48	0.37	1.16	YES	4.09	4.06	3.54	3.85	3.51	4.50	3.56
Naphthalene	5	4.76	95.17	0.56	1.77	YES	5.48	4.61	4.77	5.16	4.82	4.81	3.66
1,2,3-Trichlorobenzene	5	4.77	95.50	0.66	2.08	YES	5.76	4.80	4.49	4.82	4.29	5.43	3.83

Method: VPH
Matrix Water
Analysis Date: 9/16/02
Analyst: NM

Compound	Reporting Limit ug/L	Spike level ug/L	%Recovery	Mean ug/L	Std Dev	MDL	MDL<Spike?	1398.d	1399.d	1400.d	1401.d	1402.d	1403.d	1404.d
Methyl-tert-butyl-ether	2	1.5	121.4	1.82	0.10	0.30	yes	1.73	1.90	1.71	1.89	1.83	1.95	1.73
Benzene	2	0.5	153.9	0.77	0.09	0.28	yes	0.82	0.79	0.77	0.59	0.75	0.86	0.81
Toluene	2	1.5	113.7	1.71	0.23	0.72	yes	1.33	1.48	1.70	1.79	1.99	1.85	1.79
Ethyl Benzene	2	0.5	86.0	0.43	0.03	0.10	yes	0.48	0.44	0.45	0.38	0.44	0.40	0.41
Xylene (m&p)	2	2.0	87.5	1.75	0.12	0.37	yes	1.76	1.63	1.95	1.86	1.69	1.65	1.71
o-Xylene	2	1.0	91.6	0.92	0.07	0.21	yes	0.94	0.91	0.93	0.78	0.99	0.92	0.94
Naphthalene	5	1.0	132.6	1.33	0.10	0.30	yes	1.31	1.52	1.31	1.29	1.23	1.37	1.26

Range	Spike level ug/L	Mean ug/L	Std Dev	MDL ug/L	MDL<Spike? Yes or No?	1406.d	1407.d	1408.d	1409.d	1410.d	1411.d	1412.d	1413.d
C5-->C8	1	109.495	6.200228106	19.4687163	1	110.15	111.21	121.94	107.18	104.85	101.93	113	105.7
	total				yes								
C9-->C12	250ppb	3.27125	2.436786159	7.65150854	total 250ppb	3.41	2.57	8.89	2.44	2.37	1	3.81	1.68
	1				1								
C9-->C10	1	57.575	2.022106398	6.34941409	1	58.93	55.74	54.91	55.04	58.17	59.81	58.51	59.49
	total	170.34125	10.65912066	33.4696389		172.49	169.52	185.74	164.66	165.39	162.74	175.32	166.87
	btex cmps	50.6575				50.54	50.59	50.54	50.35	52.19	49.15	50.79	51.11
	%recovery	88.3995				89.212	88.044	94.512	86.004	87.032	84.756	90.444	87.192

EPH RANGES IN WATER MDL STUDY FOR 2002 ON SV-2

EPH 1.0 MODIFIED (REV.2) MDL STUDY USING EPA WP681 API REFERENCE FUEL OIL #2 *
250 UG SPIKE IN 1L WATER, EXTRACTED 01/09/02
ANALYZED ON SV-2 BY RKK, 1/21/02, FILES 2B19894.D TO 2B19902.D, ALL RESULTS IN UG/L

* 57.2% ALIPHATIC, 41.8% AROMATIC, EST. 81.7% C9-C18 ALIPHATICS, 18.3% C19-C36 ALIPHATICS

MDL STUDY

COMPOUNDS	#1	#2	#3	#4	#5	#6	#7	AVE	STD	MDL	MEANREC	RL	ML
C9-C18 ALIPHATICS	76.34	114.68	92.56	88.79	100.67	93.95	108.14	96.45	12.72	39.99	74.61	100	127
C19-C36 ALIPHATICS	27.88	33.08	22.76	23.13	31.36	31.58	33.83	29.09	4.60	14.45	111.14	100	46
C11-C22 AROMATICS	58.99	81.23	86.79	77.92	91.95	82.93	99.89	82.81	12.81	40.27	79.25	100	128

AVG. TOT. ALPHATIC FRACTION RECOVERY= 88%, AVG. TOT. FUEL REC.= 83%

EPH 1.0 MODIFIED (REV.2) MDL STUDY USING 0.2ML SPIKE S010702C @ 1UG EACH SINGLE ANALYTE PER 1L DI WATER,
EXTRACTED 01/09/02 USING EPA 3510
ALL RESULTS IN UG/L UNITS
ANALYZED USING SV-2 BY RKK ON 01/21/02, DATA FILES #1=2B19886.D, #2=2B19887.D, #3=2B19888.D, #4=2B19889.D, #5=2B19890.D, #6=2B19891.D, #7=2B19892.D, #8=2B19893.

MDL STUDY

COMPOUNDS	#1	#2	#3	#4	#5	#6	#7	#8	AVE	STD.DEV.	MDL	MEAN R	MDL	RL	#1 RAW
NONANE	0.385	0.45	0.34	0.37	0.305	0.29	0.33	0.29	0.345	0.0550	0.17276	34.5	0.165	1	0.89
DECANE	0.385	0.43	0.425	0.38	0.385	0.345	0.415	0.39	0.394	0.0280	0.08787	39.4	0.084	1	1.18
DODECANE	0.38	0.485	0.485	0.46	0.42	0.395	0.515	0.505	0.456	0.0512	0.16102	45.6	0.154	1	1.14
NAPHTHALENE	0.495	0.565	0.525	0.555	0.52	0.505	0.53	0.53	0.528	0.0233	0.07320	52.8	0.070	1	1.45
2-METHYLNAPHTHALEN	0.48	0.515	0.475	0.495	0.465	0.46	0.49	0.545	0.491	0.0281	0.08828	49.1	0.084	1	1.38

EPH SOIL MDL STUDY RANGE ANALYTES 2002 for SV-2

EPH 1.0 MODIFIED (REV.2) MDL STUDY USING EPA WP681 API REFERENCE FUEL OIL #2 *
2500 UG SPIKE ON 20G OTTAWA SAND, EXTRACTED 01/09/02 USING EPA 3541
ANALYZED 01/11/02 ON SV-2 BY RKK/GG, FILES 2B19803.D TO 2B19810.D, ALL RESULTS IN MG/KG

* 57.2% ALIPHATIC, 41.8% AROMATIC, EST. 81.7% C9-C18 ALIPHATICS, 18.3% C19-C36 ALIPHATICS

MDL STUDY

COMPOUNDS	Units	#1	#2	#3	#4	#5	#6	#8	AVG	STDEV	MDL	MEAN REC	PIKE CONC	RL	ML
C9-C18 ALIPHATICS	mg/kg	60.58	61.82	59.29	63.10	61.08	53.64	57.69	59.60	3.15	9.90	102.06	58.4	50	31.5
C19-C36 ALIPHATICS	mg/kg	8.47	8.74	7.28	7.54	7.56	10.76	11.41	8.82	1.64	5.17	67.36	13.1	50	16.4
C11-C22 AROMATICS	mg/kg	40.57	55.24	50.95	54.87	50.98	44.37	50.57	49.65	5.37	16.88	95.48	52.2	50	53.7