4091H

00000187

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION V

DATE: October 29, 1987

SUBJECT: Approval of Quality Assurance Project Plan for Remedial Investigation/ Feasibility Study at the National Presto Industries, Inc. Site, Wisconsin

FROM: James H. Adams, Jr., Chief
Quality Assurance Office

TO: Norman Niedergang, Chief
CERCLA Enforcement Section

ATTENTION: Mike Gifford, RPM

Our Office is returning a copy of an approved Quality Assurance Project Plan (QAPP) for Remedial Investigation/Feasibility Study at the National Presto Industries, Inc. Site, Eau Claire, Wisconsin, which our Office received on October 28, 1987 (QAO #447). The approval of this subject QAPP is provided after our Office has made the following changes:

1. Change made on 3 pages (attached).

2. Replace the SAS for the analysis of low level volatile organics, which is not applicable to laboratory for PRP project, with the 26 pages Standard Operational Procedures (SOP) prepared by Dr. Cheng-Wen Tsai, Chemist, QAO staff (attached).

Our Office has provided the special effort to prepare the SOP in order to expedite the approval of this subject QAPP. A copy of the changed page and the SOP has been inserted in the returning QAPP, and an extra copy is attached for your reference and use. Hazleton Laboratory is required to use the instrumental conditions specified in the SOP; and is also required to clearly document any deviations from the specified instrumental conditions and/or QC requirements, and be part of the data reporting package.

The original of signature page is included. Please have the Remedial Project Manager provide final sign off. We have retained a copy of this subject QAPP for our records; however, we would like to receive a copy of the complete signature page when it is available.

Attachments

cc: K. Chiu, ERRB

Pages should be removed from the OAP

U.S. Environmental Protection Agency
LP Sample Management Office
. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number
2677-E

Approved by
10/9/86

SPECIAL ANALYTICAL SERVICES
Client Request

RECEIVED
EXPRESS
JAN 20 1987

[XX] Regional Transmittal [ ] Telephone Request

. EPA Region/Client: V / HLA Madison

. RSCC Representative: Dennis Wesolowski

.. Telephone Number: (312) 886-1971

. Date of Request:

.. Site Name:

lease provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue esponse on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis of drinking water / residential wells - for volatiles, semi-volatiles and pesticide/PCB with low sensitivity limits.

. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Rev. 3.0

4. Estimated date(s) of collection: _____

5. Estimated date(s) and method of shipment: _____

6. Number of days analysis and data required after laboratory receipt of samples:

7 days for analysis. Final report and data due within 15 days of sample receipt.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Organic Analysis IFB WA85-J664

8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.): _____

1. Exceptions to Organic IFB - Attachment I

2. Required low level sensitivity limits - Attachment II

3. Requirements for determining sensitivity limits: Easily recognizable spectra for all compounds using 10 ng injection for ABNs and 1.5 ug/L for VOAs.

4. Initial calibrations: %RSD for RFs should be <40 for each VOA and ABN compound before beginning analyses.

5. Continuing calibration: Run daily calibration standard before running analyses. %D should be <25 for all compounds in both VOAs and ABNs. If some are greater, they should be reinjected. If still out, rerun 3 point curve.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

All deliverables included in the IFB are required including instrument sensitivity determinations.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: _____

Phone: _____

I. DATA REQUIREMENTS

Parameter:	Detection Limit	Precision Desired (± or Conc.)
Organics	See Attachment II	Attachment I

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (± Conc.)
Organics - As in IFB	As in IFB	Attachment I

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Contact Chuck Kile or Dennis Wesolowski

(312) 353-9087 (312) 886-1971

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

Attachment I

VOA - Increase sample volume up to 20 ml to meet sensitivity limits.

Initial Calibration: 5ug/L, 10ug/L, 20ug/L.
Continuing Calibration: 10ug/L except all those compounds that have a detection limit greater than 3.0ug/L which are to be run at 50ug/L. Acrolein and acrylonitrile can be run at 300ug/L.

Surrogates: As in IFB but at 10 ug/L with a recovery of 80 - 120%.

Matrix spike: As in IFB but at 10 ug/L with percent recovery 80 - 120%.

SPCC and CCC criteria will not be required. All RFs must be $\geq$0.05.

ABN - Extract Entire 1/2 gallon bottle - rinse cap & bottle - add to sample vol.

Decrease extract volume to help meet sensitivity limits.

Initial Calibration: 20, 50, and 100 total nanograms.

Continuing Calibration: 20 nanograms except for the following:

Benzoic acid, 2,4 - dinitrophenol, 2,4,5-trichlorophenol, all three nitroaniline isomers, 4-nitrophenol, 4,6-dinitro-2-methylphenol and pentachlorophenol which are to be injected at 50 nanograms.

Surrogates: 20 ppb BN compounds with % recoveries as listed in IFB.

40 ppb Acid compounds with % recoveries as listed in IFB.

Matrix Spike: 20 ppb BN compounds with % recoveries as listed in IFB.

40 ppb Acid compounds with % recoveries as listed in IFB.

SPCC and CCC criteria will not be required. All RFs must be $\geq$0.05.

Extract Entire 1/2 gallon bottle - rinse cap & bottle - add to sample.

Pesticide/PCB - Decrease extract volume to help meet sensitivity limits.

Calibration: As in IFB using an attenuation setting capable of achieving the sensitivity limits in Attachment II. 72 hour run sequence as in IFB.

Surrogate: As in IFB.

Matrix Spike: As in IFB.

These are the pages being changed

APPENDIX A

STANDARD OPERATIONAL PROCEDURE

FOR

THE ANALYSIS OF VOLATILE ORGANICS WITH LOW DETECTION LIMITS

BY PURGE AND TRAP GAS CHROMATOGRAPHY/MASS SPECTROMETRY METHOD

NATIONAL PRESTO INDUSTRIES, INC.
EAU CLAIRE, WISCONSIN

TABLE III-1

ANALYTES AND DETECTION LIMITS

I.	Volatiles in Water - GC/MS Low Level VOA Method (Hazleton)	CAS Number	Hazleton Detection Limits Water (ug/L)
1.	Chloromethane	74-87-3	.712
2.	Bromomethane	74-83-9	.223
3.	Vinyl Chloride	75-01-4	.423
4.	Chloroethane	75-00-3	.924
5.	Methylene Chloride	75-09-2	.747
6.	Acetone	67-64-1	.697
7.	Carbon Disulfide	75-15-0	.255
8.	1,1-Dichloroethene	75-35-4	.289
9.	1,1-Dichloroethane	75-35-3	.238
10.	trans-1,2-Dichloroethene	156-60-5	.217
11.	Chloroform	67-66-3	.269
12.	1,2-Dichloroethane	107-06-2	.176
13.	2-Butanone	78-93-3	1.000
14.	1,1,1-Trichloroethane	71-55-6	.876
15.	Carbon Tetrachloride	56-23-5	.303
16	Vinyl Acetate	108-05-4	1.100
17	Bromodichloromethane	75-27-4	.279
18	1,1,2,2-Tetrachloroethane	79-34-5	.392
19	1,2-Dichloropropane	78-87-5	.309
20	trans-1,3-Dichloropropene	10061-02-6	.240
21	Trichloroethene	79-01-6	.206
22	Dibromochloromethane	124-48-1	.268
23	1,1,2-Trichloroethane	79-00-5	.262
24	Benzene	71-43-2	.248
25	cis-1,3-Dichloropropene	10061-01-5	.385
26	2-Chloroethyl Vinyl Ether	110-75-8	.355
27	Bromoform	75-25-2	.280
28	2-Hexanone	591-78-6	.479
29	4-Methyl-2-Pentanone	108-10-1	.541
30	Tetrachloroethene	127-18-4	.254
31	Toluene	108-88-3	.244
32	Chlorobenzene	108-90-7	.182
33	Ethyl Benzene	100-41-4	.150
34	Styrene	100-42-5	.266
35	Total Xylenes	--	.274

Low Level HSL Voa Analyses
(CLP SOW Modification)

The following modifications have been made to the analytical protocol specified in the CLP SOW for RAS (organic analyses IFB WA85-J664) to achieve lower detection limits for each of the analytes.

- Purge volume: increase to 25 mL
- Initial calibration: 0.5, 2, 5, 20 and 50 µg/l. Percent RSD for RFs should be less than 40 for each compound.
- Continuing calibration: 10 µg/l; analyze daily before analyzing samples; percent D should be less than 25 for each compound.
- Surrogates: as in IFB but at 10 µg/l with recoveries of 80% to 120%.
- Matrix spike: as in IFB but at 10 µg/l with recoveries of 80% to 120%.
- Internal standards: as in IFB but at 10 µg/l.
- SPCC and CCC: not required; all RFs must be greater than 0.05.

These modifications are identical to those specified by Region V under SAS for the analyses of drinking water/residential wells. Using the above modification, the method detection limits were determined and are documented on the attachment.

(03901/lma)

10.1.2.1 If any compound in any sample exceeds the initial calibration range, that sample must be diluted, the internal standard concentration readjusted, and the sample reanalyzed. Secondary ion quantitation is only allowed where there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the Case Narrative.

10.1.2.2 If the dilution of the sample causes any compound detected in the first analysis to be undetected in the second analysis, then the results of both analyses shall be reported.

10.2 Analysis Procedure

10.2.1 At the beginning of each date that analyses are to be done, acceptable performance criteria must be achieved by BFB. This performance test must be passed before any samples, blanks or standards are analyzed. The performance test should be done under the following instrument parameters:

Electron energy = 70 V (nomimal)
Mass range = 20 to 260 AMU
Scan Time = To give at least 5 scans per peak but not to exceed 7 sec. per peak.

10.2.2 Sample purging

10.2.2.1 Set up the purge and trap system

Adjust the purge gas (helium) flow rate to 40 ml/min. Set up the purge and trap system to purge.

10.2.2.2 Fill the purging device

Allow the sample to come to ambient temperature prior to introducting it into the syringe.

a) Remove the plunger from a 25 ml syringe and attach a closed syringe valve.

b) Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing.

c) Replace the syringe plunge and compress the sample.

d) Hold the syringe in upright position with the syringe value set on top of the syringe. Open the syringe valve and vent any residual air while adjusting the sample volume to 25 ml.

e) Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data.

f) Add 10.0 ul of the surrogate spike solution and 10.0 ul of the internal standard spiking solution through the valve bore, then close the valve.

g) Attach the syringe-syringe valve assembly to the syringe valve on the purging device.

h) Open the syringe valves and inject the sample into the purging chamber. Close both valves.

10.2.2.3 Purging

a) Purge the sample for 11.0 $\pm$0.1 minutes at ambient temperature.

b) After the 11 minutes purge time, attach the trap to the chromotograph, adjust the purge and trap system to the desorb mode.

10.2.3 Gas Chromotography/Mass Spectrometry Analysis

a) Setting up GC/MS operating parameters.

Carrier gas flow rate - 40 ml/min
Injector temperature - 220°C
Oven temperature - hold at 45°C for 3 minutes then heated to 220°C at 8°C/min, then held at 200°C until the programmed run time expires.
Transfer line temperature - 225°C
Ion source temperature - 220°C
Scan range - 40-250 amu
Electron energy - 70 V

b) Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas between 20 and 60 ml/min for 4 minutes. If rapid heating of the trap can not be achieved, the GC column must be used as a second trap by cooling it to 30°C, or subambient temperature (cryogenic trapping) if problem persist, instead of the initial program temperature of 45°C.

c) While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 25-ml flushes of reagent water.

d) After desorbing the sample from trap for 4 minutes, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. After 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

e) If the response for any $m/_z$ exceeds the working range of the system, prepare dilution of the sample with reagent water from the aliquot in the second syringe and reanalyze.

10.2.4 Qualitative Identifcation

Obtain extracted Ion current profiles (EICPs) for the primary $m/_z$ (Table 6) and at least two secondary masses for each parameter of interest. The following criteria must be met:

a) The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

b) The retention time must fall within ±130 seconds of the retention time of the authentic compound.

c) The relative peak heights of the three characteristic masses in the EICPs must

fall within ±20% of the relative intensity of these masses in a reference mass spectrum.

10.2.5 Quantitation and Calibration

10.2.5.1 When a parameter has been identified, the quantitation of that parameter should be based on the intergrate abundance from the EICPs of the primary characteristic $m/_z$ given in Table 6.

10.2.5.2 Use Equation 4 to calulate the concentration in the sample using the response factor (RF) determine in Section 7.2.1.

$$\text{Con. (ug/L)} = \frac{As \times C_{IS}}{A_{IS} \times RF} \qquad \text{Eq.6}$$

where As = Area of the characteristic $m/_z$ for the parameter or surrogate standard to be measured.

Ais = Area of the characteristic $m/_z$ for the internal standard.

Cis = Concentration of the internal standard.

10.2.5.3 Report result in ug/l without correction for recovery data. All QC data obtained should be reported with the sample results.

TABLE 6

CHARACTERISTIC MASSES FOR PURGEABLE ORGANICS

Parameters	Primary	Secondary
Chloromethane	50	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49,51,86
Trichlorofluou methane	101	103
1,1-dichloroethene	96	61,98
1,1-dichloroethane	63	65,83,85,98,100
Trans 1,2-dichlormethane	96	61,98
Chloroform	83	85
1,2-dichloroethane	98	62,64,100
1.1.1-trichloroethane	97	99,117,119
Carbontetrachloride	117	119,121
Bromodichloromethane	127	83,85,129
1.2-dichloropropane	112	63,65,114
Trans-1.3-dichloropropane	75	77
Trichloroethene	130	95,97,132
Benzene	78	
Dibromochloromethane	127	129,208,206
1.1.2-trichloroethane	97	83,85,99,132,134
Cis-1.3-dichloropropene	75	77
2-Chloroethyl vinyl ether	106	63,65
Bromoform	173	171,175,250,252,254,256
1.1.2.2-tetrachloroethane	168	83,85,131,133,166
Tetrachloroethene	164	129,131,166
Toluene	92	91
Chlorobenzene	112	114
Ethylbenzene	106	91
1,3-dichlorobenzene	146	148,113
1,2-dichlorobenzene	146	148,113
1.4-dichlorobenzene	146	148,113

APPENDIX A

STANDARD OPERATIONAL PROCEDURE

FOR

THE ANALYSIS OF VOLATILE ORGANICS WITH LOW DETECTION LIMITS BY PURGE AND TRAP GAS CHROMATOGRAPHY/MASS SPECTROMETRY METHOD

PREPARED BY

CHENG-WEN TSAI, CHEMIST

QUALITY ASSURANCE OFFICE

OCTOBER 19, 1987

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TABLES

ANALYSIS OF VOLATILE ORGANICS WITH LOW DETECTION LIMITS BY PURGE AND TRAP GAS CHROMATOGRAPHY/MASS SPECTROMETRY METHOD

(PREPARED BY CHENG-WEN TSAI)

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of the following 36 purgeable organics.

Parameter	CAS Number
Chloroethane	75-00-3
Benzene	71-43-2
Bronodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
2-Chloroethyl vinyl ether	100-75-8
Chloroform	67-66-3
Chloromethane	74-87-3
Dibromochloromethane	124-48-1
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-1
1,1-Dichloroethane	75-34-3
1,2-Dichloroethene	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-2
thrans-1,2-Dichloroethene	156-60-5
Dichloromethane	75-09-2
1,2-Dichloropropane	78-87-5
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene	100-41-4
Styrene	100-42-5
1,1,2,3-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichloroflouromethane	75-69-4
Vinyl chloride	75-01-4
o--XYlene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

1.2 This is a purge and trap gas chromatrography/mass spectrometry (GC/MS) method applicable to the determination of the compounds listed above in municipal (drinking) water, groundwater and industrial waste water.

1.3 The method detection limit (MDL) for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of the interferences in the sample matrix.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system and gas chromatograph/mass spectrometry and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 10.

2.0 SUMMARY OF METHOD

2.1 An inert gas is bubbled through a 25-ml water sample contained in a specially designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatrographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

3.0 INTERFERENCES

3.1 Impurities in the purge gas, organic compounds outgassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contaimination under the conditions of the analysis by running laboratory reagent blanks. The use of non-telfon plastic tubing, non-Teflon trhread sealants, or flow controllers with rubber components in the purge and trap system should be avoided.

TABLE 1

ANALYTES AND DETECTION LIMITS
by GC/MS Method

PARAMETER	CAS NUMBER	DETECTION LIMITS WATER (ug/L)
1. Chloromethane	74-87-3	.712
2. Bromomethane	74-83-9	.223
3. Vinyl Chloride	75-01-4	.423
4. Chloroethane	75-00-3	.924
5. Mythylene Chloride	75-09-2	.747
6. Acetone	67-64-1	.697
7. Carbon Disulfide	75-15-0	.255
8. 1,1-Dichloroethene	75-35-4	.289
9. 1,1-Dichloroethane	75-35-3	.238
10. trans-1,2-Dichloroethene	156-60-5	.217
11. Chloroform	67-66-3	.269
12. 1,2-Dichloroethane	107-06-2	.176
13. 2-Butanone	78-93-3	1.000
14. 1,1,1-Trichloroethane	71-55-6	.876
15. Carbon Tetrachloride	56-23-5	.303
16. Vinyl Acetate	108-05-4	1.100
17. Bromodichloromethane	75-27-4	.279
18. 1,1,2,2-Tetrachloroethane	79-34-5	.392
19. 1,2-Dichloropropane	78-87-5	.309
20. trans-1,3-Dichloropropene	10061-02-6	.240
21. Trichloroethene	79-01-6	.206
22. Dibromochloromethane	124-48-1	.268
23. 1,1,2-Trichloroethane	79-00-5	.262
24. Benzene	71-43-2	.248
25. cis-1,3-Dichloropropene	10061-01-5	.385
26. 2-Chloroethyl Vinyl Ether	110-75-8	.355
27. Bromoform	75-25-2	.280
28. 2-Hexanone	591-78-6	.479
29. 4-Methyl-2-Pentanone	108-10-1	.541
30. Tetrachloroethene	127-18-4	.254
31. Toluene	108-88-3	.244
32. Chlorobenzene	108-90-7	.182
33. Ethyl Benzene	100-41-4	.150
34. Styrene	100-42-5	.266
35. Total Xylenes	--	.274

3.2 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocal can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging devide and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusally concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. It may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses. The trap and other parts of the system are also subjected to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4.0 SAFETY PRECAUTIONS

4.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected human or mammalian carcinorgens: benzene, 1,4-dichlorobenzene, hexachlorobutadiene, tetrachloroethene, trichloroethene, carbon tetrachloride, bis-2-chloroisopropyl ether, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromomethane and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. NIOSH/MESA approved toxic gas respirator should be worn when the analysts handle high concentrations of these toxic compounds.

5.0 APPARATUS AND MATERIALS

5.1 Sample containers

Forty milliliter (40-ml) screw cap vials with PTFE-faced silicone septum seals. Wash vials and seals with detergent, rinse with tap water, then distilled water, and dry at 105°C, allow to cool in area known to be free of organic vapors.

5.2 Purge and Trap System (Tekmar LSC-2 or equivalent)

5.2.1 Purging Device

The all glass purging device must be capable of accepting 25-ml samples with a water column at least 5-cm deep. A glass frit installed at the base of sample chamber allowing purging gas to pass through the water column as finely divided bubbles with a diameter of 3 cm at the origin.

5.2.2 Volatile Trap

The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inches. The trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. Prior to daily use, the trap is conditioned for 10 minutes at 220°C while backflushing with an inert gas flow of at least 20 ml/min. The trap effluent is vented to the room through a charcoal trap.

5.2.3 Desorber

The desorber must be capable of rapidly preheating the trap to 180°C, then desorbing the trap to the GC column while maintaining the temperature of 180°C.

5.3 GC/MS SYSTEM

5.3.1 Gas chromatograph (Hewlet Parkard 5993 GC or equivalent)

GC must be capable of temperature programming and achieving an initial column temperature of 30 - 45°C. Veriable constrant differential flow controllers capable of maintaining constant flow rates throughout the desorbtion and temperature program should be used.

5.3.2 Gas Chromatography Column

Eight ft. long x 1/8 O.D. glass column, packed with 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent.

5.3.3 Mass Spectrometer (Finnigan 5100 MS or equivalent)

Must be capable of scanning from 20 to 260 amu every 7 s or less, utilizing 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meet all the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet.

5.3.4 GC/MS Interface

GC to Ms interface constructed of all glass or glass-lined materials should be used. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.3.5 Data System

A computer system must be interfaced to the mass spectrometer that allows the continuours acquisition and storage on machine-readable media of all mass spectra obtained through the duration of the chromatographic program. The computer must have the software that allows searching any GC/MS data file for specific m/z (masses) and plotting such m/z abundance versus time or scan number. Software must also allow integrating the abundance in any Extracted Ion Current Profile (EICP) between specific time or scan number limits.

5.3.6 Syringe and Syringe Valves

5.3.6.1 Syringes - 5-ml and 25-ml glass hypodermic with luerlock tip (two each).
5.3.6.2 Micro Syringes - 25 and 100 ul.
5.3.6.3 Gas syringes - 1.0 and 5.0 ml gas tight, with shut off valve.

5.3.7 Miscellaneous

5.3.7.1 Standard Storage Containers - 3.7 ml Screw cap amber vials.
5.3.7.2 Mininert valuves- screw cap.

6.0 REAGENTS

6.1 Methanol, demonstrated to be free of analytes (spike 100 ul into 25-ml reagent water and analyze. Should produce less than 0.4 ug/L response).

6.2 Reagent water, producing less than 0.2 ug/L response for those compounds that are monitoried. Prepare by boiling distilled or natural waters for 15 minutes followed by 1-h purge with inert gas while temperature is held at 90°C or carbon filtered. Store in clean, narrow mounthed crip top PTFE-lined septa bottles.

6.3 Stock standard: Commerical mixed stock solutions are available (Supelco Purgeables A, B, and C) that contain most of the compounds of interest at a concnetration of 0.2 mg/mL. Stock solutions must be prepared from neat, as follows for those compounds not included in the commerical mixes. (1)

6.3.1 Methanol (24.4 mL) is placed in a 25-mL volumetric flask. Allow flask to stand unstoppered for 10 minutes or until all alcohol-wetted surfaces have dried and tare.

6.3.2 Using a 100-uL syringe, add 50 mg of assayed reference material to the flask. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask. Retare the flask and add 50 mg of the next compound. Repeat the process until all compounds have been added.

6.3.3 Dilute to volume, and stopper. Mix by inverting flask several times. The resulting solution will contain each analyte at a concentration of 2.0 mg/mL.

(1) The following compounds must be made from neat: Cis-1,2-Dichloroethene, o-xylene, m-xylene, p-xylene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 1,2-Dichlorobenzene, Styrene.

6.3.4 Store stock standard solutions in 3 mL vials equipped with PTFE mininert valve tops at 0°C. All standards must be replaced each month.

6.3.5 Secondary Dilution Standards. Using stock standards prepare secondary dilution standards in methanol. The secondary dilution standards are prepared at concentrations that can easily be diluted to prepare aqueous calibration standards that will bracket the working range of the method.

6.3.5.1 To prepare secondary dilution standards, place 9.0 mL of methanol into a 10 mL volumetric flask.

6.3.5.2 Inject exactly 250 uL of the Supelco Purgeable A stock solution, and 25uL of the stock solution prepared from neat (above) into the methanol. When prepared as above, the solution will contain each analyte at a concentration of 5 ng/uL.

6.3.5.3 Separate secondary dilution standards mixture should be prepared weekly for the gases from the Supelco Purgeables C mix.

6.3.5.4 Store secondard dilution standards in 3-mL glass vials equipped with PTFF mininert valve screw tops. Storage conditions and times described for stock standard solutions also apply to secondary dilution standard solutions.

6.4 Sample spiking solution:

Place a 9.5 mL of methanol into a 10 ml volumetric flask, add 250 uL of Supelco purgeable A and 250 ul of Supelco Purgeable B. Dilute to volume and mix. The resulting solution will contain the analytes listed in Table 2 at a concentration of 5 ng/ul. Store at 0°C. The sample spiking solution should be discarded after 1 month.

6.5 Internal surrogate standard:

Prepare from neat bromochloromethane (50 mg) and flourobenzene (125 mg) as in Section 6.3 above. The resulting stock solution will contain bromochloromethane at 2.0 mg/mL and flourobenzene at 5.0 mg/mL.

6.5.1 Dilute 25 ul of stock in 25 mL of methanol. The internal surgogate standard when prepared as above will contain bromochloromethane at a concentration of 2 ng/ul and flourobenzene at a concentration of 5 ng/ul.

TABLE 2

Listing of Compounds Found in Matrix Spiking Solution

Trans-1,2-Dichloroethylene
1,2-Dichlotoethane
1,1,1-Trichloroethane
Bromodichloromethane
Trans-1,3-Dichloropropene
Cis-1,3-Dichloropropene
Benzene
Bromoform
1,1,2,2-Tetrachloroethane
Toluene
Ethyl Benzene
Trichloroethylene
1,1,2-Trichloroethane
Dibromochloromethane
2-Chloroethyl vinyl ether
Tetrachloroethylene
Chlorobenzene
Methylene Chloride
Trichloroflouromethane
1,1-Dichloroethylene
1,1-Dichloroethane
Chloroform
1,2-Dichloropropane

7.0 CALIBRATION AND STANDARDIZATION

7.1 Tuning and GC/Ms Mass Calibration

7.1.1 The laboratory must establish that a given GC/MS system meet the standard spectral abundance criteria prior to initiating any on-going data collection. The GC/MS system must be hardware tuned to meet the abundance criteria listed in Table 3 for a maximum of a 50 ng injection of 4-Bromofluorobenzene (BFB). Add 50 ng of BFB solution to 25 ml of reagent water and analyze alone. BFB should not be analyzed simultaneously with any calibration standards or blanks. This criteria must be demonstrated daily or for each twelve-hour time period. If required, background substraction must be straight forward and designed only to eliminate column bleed or instrument background.

7.1.2 BFB criteria must be met before any standards, samples or blanks are analyzed.

7.1.3 Any action taken which may result in effecting the tuning criteria for BFB, the tune must be verified irrespective of the twelve-hour tuning requests.

7.1.4 The laboratory shall document the GC/MS tuning and mass calibration each time the system is tuned.

7.2 Calibration of GC/MS System

7.2.1 Initial Internal Standard Calibration

7.2.1.1 Prior to the analysis of samples and reguired blanks, and after tuning criteria have been met, the GC/MS system must be initially calibrated at a minimum of five concentrations to determine the linearity of response utilizing TCL compound standards. Once the system has been calibrated, the calibration must be verified each twelve (12) hour time period for each GC/MS system.

TABLE 3

BFB KEY IONS AND ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15.0 - 40.0 percent of the base peak
75	30.0 - 60.0 percent of the base peak
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of base peak
173	less than 2.0 percent of mass 174
174	greater than 50.0 percent of the base peak
175	5.0 - 9.0 percent of mass 174
176	greater than 95.0 percent but less than 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

7.2.1.2 Prepare calibration standards to yield the following specific concentrations: .5, 2, 5, 20 and 50 ug/l. Surrogate and internal standards shall be used with each of the calibration standards.

7.2.1.3 Analyze each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including all required surrogate compounds. The relative retention time (RRT) of each compound in each calibration run should agree within o.06 RRT units.

7.2.1.4 Use Table 4 and Equation 1 to calculate the relative response factors (RRF) for each compound at each concentration level.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x} \qquad \text{Eq. 1}$$

where,

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the specific internal standards from Table 2.

C_{is} = Concentration of the internal standard (ng/uL).

C_x = Concentration of the compound to be measured (ng/uL).

7.2.1.5 Use equation 2 and the relative response factors (RRF) from the initial calibration to calibrate the relative standard deviation (% RSD) for compounds labelled as calibration check compounds in Table 4.

$$\%RSD = \frac{SD}{\bar{x}} \times 100 \qquad \text{Eq. 2}$$

where,

RSD = Relative Standard Deviation

TABLE 4

VOLATILE INTERNAL STANDARDS WITH CORRESPONING
TCL ANALYTES ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d_5
Chloromethane	2- Butanone	2-Hexanone
Bromomethane	1,1,1-Trichloroethane	4-Methyl-2-Pentanone
*Vinyl Chloride	Carbon Tetrachloride	Tetrachloroethene
Chloroethane	Vinyl Acetate	1,1,2,2-Tetrachloroethane
Methylene Chloride	Bromodichloromethane	*Toluene
Acetone	*1,2-Dichloropropane	Chlorobenzene
Carbon Disulfide	trans-1,3-Dichloropropane	*Ethylbenzene
*1,1-Dichloroethene	Trichloroethene	Styrene
1,1-Dichloroethane	Dibromochloromethane	Xylene (total)
1,2-Dichloroethene (total)	1,1,2-Trichloroethane	Bromofluorobenzene (surr)
*Chloroform	Benzene	
1,2-Dichloroethane	cis-1,3-Dichloropropene	Toluene-d_8 (surr)
1,2-Dichloroethane-d_4 (surr)	Bromoform	

(surr) = surrogate compound
*Calibration check compounds

SD = Standard Deviation of initial relative response factors (per compound)

where: $$SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N-1}}$$ Eq. 3

$\bar{x}$ = mean of initial relative response factors (per compound)

The %RSD for each individual Calibration Check Compound must be less than or equal to 30.0 percent. This criteria must be met for the initial calibration to be valid.

7.2.1.6 System Performance Check

A system performance check must be performed to insure that minimum average relative response factors are met before the calibration curve is used. This is done by analyzing five system performance check compounds (SPCCs): Chloromethane, 1,1-dichloroethane, bromoform, 1.1.2.2 -tectrachloroethane and chlorobenzene. The minimum acceptable RRF for these compounds is 0.300 (0.250 for bromoform).

7.2.1.7 The initial calibration is valid only after both the %RSD for calibration check compounds and the minimum RRF for SPCC have been met. Only after both these criteria are met can sample analysis begin.

7.3 Continuing Calibration Check

7.3.1 A calibration standard(s) containing all volatile TCL compounds, including all required surrogates, must be performed each twelve hours during analysis. (The concentration for each TCL compounds in the CCC is 20 ug/l). Compare the relative response factor data from the standards each twelve hours with the average relative response factor from the intital calibration for a specific instrument. A system performance check must be made each twelve hours. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds.

7.3.2 After the system performance check is met, use Equation 4 to caliculate the percent difference (% difference) for all calibration check compounds in Table 4 in order to check the validity of the initial calibration.

7.3.2.1 Calculate the percent difference using Equation 4.

$$\% \text{ Difference} = \frac{\overline{RRF}_I - RRF_C}{RRF_I} \times 100 \qquad \text{Eq. 4}$$

where

$\overline{RRF}_I$ = average relative response factor from initial calibration

RRF_C = relative response factor from current calibration check standard

7.3.2.2 If the percent difference for any compound is greater than 20%, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than or equal to 25.0%, the initial calibration is assumed to be valid. If the criteria are not met (>25.0% difference), for any one calibration check compound, corrective action MUST be taken. Problems similar to those listed under SPCC could affect this criteria. If no source of the problem can be determined after corrective action have been taken, a new initial five point calibration MUST be generated. These criteria MUST be met before sample analysis begins.

8.0 QUALITY CONTROL

8.1 The performance of the entire analytical system can be checked daily using the data collected from the analysis of method blanks, field blanks, sample matrix spikes, sample matrix spike duplicates, and calibration check standards.

8.1.1 Method Blank Analysis

A method blank, consists of deionized, distilled laboratory water, must be analyzed once for each 12-hour time period. The method blank volume must be approximately equal to the sample volume being processed. The laboratory must demonstrate the method blank is free of contamination.

8.1.2 Surrogate spike analysis

Surrogate standard determination are performed on all-samples and blanks. Each sample, matrix spike, matrix spike duplicate, and blanks are spiked with surrogate compounds to be used. The amount of surrogate standard to be used and the acceptable % recovery limits are tabulated in Table 5.

TABLE 5

SURROGATE SPIKE COMPOUNDS, CONCENTRATIONS AND RECOVERY LIMITS

Compounds	Concentration	% Recovery
Toluene-d_8	50 ug	88-110
4-Bromoflurorobenzene	50 ug	86-115
1,2-dichloroethane-d_4	50 ug	76-114

8.1.3 Matrix spike/matrix spike duplicate analysis

8.1.3.1 A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix, once

- each Case of field samples received, OR
- each 20 field samples in a Case, OR
- each group of samples of a similar concentration level (soils only), OR
- Each 14 calendar day period during which samples in a Case were received (said period beginning with the receipt of the first sample in that Sample Delivery Group), whichever is most frequent.

The concentration of matrix spike should be 2 times of method detection limits (MDL) if the compound is detected in the sample, otherwise 5 times of the method detection limit.

8.1.3.2 Individual component recoveries of the matrix spike are calculated using Equation 5.

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100 \qquad \text{Eq.5}$$

where,

SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added from spiking mix

8.1.3.3 Relative Percent Difference (RPD)

The contractor is required to calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using Equation 6

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100 \qquad \text{Eq.6}$$

where,

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

9.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

9.1 Sample Collection

9.1.1 Replicate trip blanks must be handled along with each sample set, which is composed of the samples collected from the same general sampling site at approximately the same time. At the laboratory, fill a minimum of two sample bottles with reagent water, seal, and ship to the sampling site along with empty sample bottles. Wherever a set of samples is shipped and stored, it must be accompanied by trip blanks.

9.1.2 Field blank sample, which is composed of deionized laboratory water, will be collected one per group of 10 or fewer samples. Field blank should be prepared in the field as following: Deionized laboratory water is allowed to be in contract with sampling equipment and then is poured into the sampling vial. No air bubbles should be trapped in the field blank sample when the vial is sealed.

9.1.3 For samples collected to determine compliance with total trinalomethane regulations (40 CFR Part 141.30), add 2.5 to 3 mg reducing agent per 40 mL to the empty sample bottles and blanks just prior to shipping to the sampling site.

9.1.4 Collect all samples in duplicate (triplicate when high levels requiring screening and dilution are suspected). FIll sample bottles to overflowing. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

9.1.5 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 minutes). Adjust the flow to above 500 mL/minute and collect duplicate samples from the flowing stream.

9.1.6 When sampling from an open body of water, fill a 1-qt wide-mouth bottle or 1-L breaker with sample from a representative area, and carefully fill duplicate sample bottles from the 1-qt container.

9.2 Sample Preservation

9.2.1 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be at 4°C on arrival at the laboratory.

9.2.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

10.0 SAMPLE ANALYSIS

10.1 Quality Control Requirements

Samples can be analyzed upon successful completion of the initial QC activities. When twelve (12) hours have elapsed since the initial tune was completed, it is necessary to conduct an instrument tune and calibration check analysis. Any major system maintenance, such as a source cleaning or installation of a new column, may necessitate a retune and recalibration irrespective of the twelve-hour requirement (see Initial Calibration). Minor maintenance should necessitate only the calibration verification (Continuing Calibration).

10.1.1 Internal Standards Evaluation - Internal standard responses and retention times in all samples must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds, the chromatographic system must be inspected for malfunctions, and corrections

made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the extracted ion current profile (EICP) area for any internal standard changes by more than a factor of two (-50% to 100%), from the latest daily (12 hour time period) calibration standard, the mass spectrometric system must be inspected for malfunction, and corrections made as appropriate. Breaking off 1 foot of the column (when using capillary column) or cleaning the injector sleeve (when using either packed or capillary column) will often improve high end sensitivity for the late eluting compounds; repositioning or repacking the front end of the column will often improve front end column performance. Poor injection technique can also lead to variable IS ratios. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

10.1.1.1 If after reanalysis, the EICP areas for all internal standard are inside the acceptable limits (-50% to +100%), then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, only submit data from the analysis with EICP's within the acceptable limits. This is considered the initial analysis and must be reported as such on all data deliverables.

10.1.1.2 If the reanalysis of the sample does not solve the problem, i.e., the EICP areas are outside the acceptable limits for both analyses, then submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables. Document in the Case Narrative all inspection and corrective actions taken.

10.1.2 Each analytical run must also be checked for saturation. The level at which an individual compound will saturate the detection system is a funtion of the overall system sensitivity and the mass spectral characteristics of that compound. The initial method calibration requires that the system should not be saturated for high response compounds at 200 ug/L for VOA TCL compounds.