PNL-MA-599

Analytical Chemistry Laboratory Department

ANALYTICAL CHEMISTRY LABORATORY (ACL) PROCEDURE COMPENDIUM

Volume 4: Organic Methods

Upon termination or transfer this manual shall be returned to
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Approved for Use
and Application by

A. G. King
Department Manager

Battelle
Pacific Northwest Laboratories
Richland, Washington

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-MA-599-Vol.4-1
Page 1 of 1

A.

Document Number: See Attachment **Revision Number:** ____

Document Title: See Attachment

Document's Original Author: See Attachment

Effective Date of ICN: 12 / 23 / 92

Change Requested by: AG King

B. **Action:** Place the attached procedures in PNL-MA-599 manual, Volume 4. Place this ICN and attachment with the Table of Contents.

C. **Effect of Change:** Incorporates the procedures from the PNL-MA-597 manual into PNL-MA-599.

D. **Reason for Change/Description of Change:**

Incorporates the procedures from PNL-MA-597 manual into PNL-MA-599 manual by changing the procedure numbers. This eliminates the need for maintaining two sets of technical procedures. Procedural references in these procedures have been updated. See attachment for the procedures to be incorporated into PNL-MA-599 manual, Volume 4.

E. **Approval Signatures:**
(Please sign and date)

Type of Change: (Check one):
X Minor ___ Major

Process Quality Department: TL Ehlert TL Ehlert **Date:** 12/23/92

Approval Authority: AG King A.G. King **Date:** 12/23/92

Other Approvals: _____ **Date:** / /

: _____ **Date:** / /

ICN- PNL-MA-599- Vol.4-1

New Doc#	Rev.	Author	Document Title	Old Doc#
PNL-ALO-383	0	DL Baldwin	Analysis of solid samples for carbonate by use of coulometrics model 5011 coulometer	7-40.36 & PNL-SP-78

PNL-MA-599 ANALYTICAL CHEMISTRY LABORATORY (ACL) PROCEDURE COMPENDIUM
Volume 4: Organic Methods

April 5, 1993

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PNL-ALO-347	1	0	SAMPLE PREPARATIONS FOR PESTICIDES/PCBS ANALYSIS IN WATER AND SOIL SEDIMENT	01/08/93
PNL-ALO-350	0	0	REPORT PREPARATION	08/03/89
PNL-ALO-360	0	1	FLORISIL COLUMN CLEAN-UP FOR PESTICIDES/PCBS ANALYSIS	09/06/91
PNL-ALO-361	0	0	SILICA GEL CLEAN-UP OF SAMPLES FOR DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS	04/26/91
PNL-ALO-362	0	0	ACID-BASE PARTITION CLEAN-UP OF SAMPLES FOR SEMIVOLATILE ORGANICS ANALYSIS	04/26/91
PNL-ALO-363	0	0	CONCENTRATE ACID WASH CLEAN-UP	04/26/91
PNL-ALO-380	0	1	DETERMINATION OF CARBON IN SOLIDS USING THE COULOMETRICS CARBON DIOXIDE COULOMETER (REPLACES PNL-SP-79)	03/06/92
PNL-ALO-381	0	0	DETERMINATION OF TC, TOC, AND TIC IN RADIOACTIVE LIQUIDS, SOILS, AND SLUDGES BY HOT PERSULFATE METHOD (REPLACES 7-40.47)	02/25/92
PNL-ALO-383	0	0	ANALYSIS OF SOLID SAMPLES FOR CARBONATE BY USE OF COULOMETRICS MODEL 5011 COULOMETER	08/01/89
PNL-ALO-384	0	0	SOXHLET EXTRACTION	01/21/93

INTERIM CHANGE NOTICE
ICN

ICN-PNL-ALO-320.2 R0
PAGE 1 OF 1

A. Document Number: PNL-ALO-320 Revision Number: 0

Document Title: Method for Extractable Organic Halides (EOX) in Solids

Document's Original Author: GA Ross

Effective Date of ICN: 10/29/92

Change Requested by: MJ Steele

B. Action:

Replace pages 1 - 9 with the attached pages 1 - 9.

C. Effect of Change:

More complete and reproducible extractions.

D. Reason for Change/Description of Change:

1) Concern that the water in the extraction procedure and the sample may cause some organic halide to remain in the aqueous phase rather than go into the extraction solvent. The removal of the water in the sample with the sodium sulfate and then not adding the additional 1 ml of water will relieve this concern. It will allow all halides to extract. See redline/strike-out in Section 9.2 and 9.3.

2) Clarify existing requirements. See redline/strike-out in Section 1.0, 2.0, 4.0 and 6.0.

3) Delete requirements for determination of dry weight due to inability to perform this determination at present in the organic laboratory. See strike-out in Section 8.3.

E. Approval Signatures
(Please sign and Date)

Type of Change (Check (✓) one)
( )Minor Change (✓)Major Change

PQ Department Concurrence: TL Ehlert T L Ehlert Date: 10/29/92

Approval Authority: AG King A. G. King Date: 12/16/92

Other Approvals: RW Stromatt [illegible] Date: [illegible]

: EW Hoppe [illegible] Date: [illegible]

Author: GA Ross G A Ross Date: 10-29-92

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-320.1-R0

A.

Document Number: PNL-ALO-320 **Revision Number:** 0

Document Title: Method for Extractable Organic Halides (EOX) in Solids

Document's Original Author: GA Ross

Effective Date of ICN: 6/22/92

Change Requested by: WT Cobb

B.

Action:

Replace pages 1 - 9 due to new format. **DO NOT REMOVE FIGURE 1 OR ATTACHMENTS.**

C.

Effect of Change:

1. Update and clarify procedure.
2. Updates procedure so an alternative injection technique may be performed properly.
3. Updates procedure so control limits for non-soil matrices may be determined.

D.

Reason for Change/Description of Change:

REASON:

1. Procedure states to use an uncontaminated soil as a blank. It is not believed this soil blank would be as accurate an indicator of method contamination/interferences as running a solvent blank. A solvent blank would indicate solvent/method contamination for all samples, while a soil blank may falsely identify contaminates/interferences for non-similar matrix types.
2. 20 µL injection of solvent using sample boat technique overloads the system causing heavy soot buildup and diminished system performance.
3. Control limits determined with a soil matrix may not be valid for non-similar matrices.

DESCRIPTION: See redline and strikeouts in Sections 6.5, 7.2 and 7.3.

E.

Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

___ Minor X Major

Process Quality Department: TL Ehlert TL Ehlert **Date:** 6/17/92

Approval Authority: AG King **Date:** 6/22/92

Other Approvals: RW Stromatt RW Stromatt 6/18/92 **Date:** 6/18/92

Author : GA Ross **Date:** 6/22/92

TITLE: PNL-ALO-320, METHOD FOR EXTRACTABLE ORGANIC HALIDES (EOX) IN SOLIDS

APPLICABILITY

This method is to be used for the determination of extractable organic halides (EOX) as Cl^- in solids. EOX is defined as the sum of those organic halides which are extracted and detected by pyrolysis/microcoulometry under the conditions specified in this method. EOX includes, but is not limited to, the priority pollutant organic halides specified in EPA Method 624 and 625. Extractable organic halides containing chlorine, bromine, or iodine are detected. However, fluorine containing species are not detected by this method.

This method has been evaluated for solid wastes, soils, and suspended solids isolated from industrial waste water.

Since this method does not identify individual components, it is advisable that compound specific techniques be employed to determine the individual components present in samples exhibiting significant EOX levels, unless the nature of the sample is already known.

DEFINITIONS

None

RESPONSIBLE STAFF

The staff responsible for implementing this procedure are:

- Cognizant Scientist
- Technician

PROCEDURE

1.0 Summary of Method

A 1-gram aliquot of solid sample is extracted with ethyl acetate by sonification ~~or vortex stirring~~ to isolate organic halides. A ~~105~~-25 μl aliquot of the extract is injected into a pyrolysis furnace using a stream of CO_2/O_2 and the hydrogen halide (HX) pyrolysis product is determined by microcoulometric titration.

Author	Date	Project Mgr.	Date	QAD Representative	Date
GA Ross		TE Jones		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
RW Stromatt		WC Weimer		SIGNATURES ON FILE	

Procedure No.	Revision No.	Effective Date	Page
PNL-ALO-320	0	April 30, 1990	1 of 9

2.0 Interferences

2.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

2.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by soaking in a 5% Contrad 70 (or equal) (product of Curtin Matheson Scientific Inc., P.O. Box 1546, Houston, Texas) solution for a minimum of 2 hours. The glassware is then rinsed with tap water, laboratory distilled water and finally with ASTM type 2 water. After drying the glassware, it can be heated in a muffle furnace at 400°C for 15 to 30 minutes to remove traces of residual organics.

Note: Volumetric glassware should not be heated in a muffle furnace.

2.1.2 The use of high purity reagents and gases helps to minimize interference problems.

2.1.3 The use of non-TFE (polytetrafluoroethylene) plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purge gas stream should be avoided.

2.2 Samples can be contaminated by diffusion of volatile organics (particularly solvents such as methylene chloride) through the septum seal into the sample during shipment and storage.

2.3 All operations should be carried out in an area where halogenated solvents, such as methylene chloride, are not being used.

2.4 Certain inorganic halide salts (e.g., mercuric chloride) will be extracted, and therefore, interfere to some extent.

3.0 Special Safety Considerations

3.1 The toxicity or carcinogenicity of each reagent in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current-awareness file of OSHA regulations regarding the safe handling of the chemicals used in this method. A reference file of material handling data sheets should also be made available to all personnel involved in the chemical analysis.

3.2 Certain EOX compounds are tentatively classified as known or suspected human or mammalian carcinogens. These include (but are not limited to) carbon tetrachloride, chloroform, 1,4-dichlorobenzene, vinyl chloride, polychlorinated biphenyls, α-BHC, β-BHC, δ-BHC, γ-BHC, and 4,4′-DDT. Primary standards of these compounds should be prepared in a hood. Handling of samples should be done in a hood.

4.0 Apparatus and Materials

(All specifications are suggested. Catalog numbers are included for illustration only.)

4.1 Sampling Equipment, for discrete sampling.

- Pre-cleaned Vial - 25 mL capacity or larger, equipped with a screw cap with teflon seal. ~~Detergent wash (Contrad 70) rinse with tap and distilled water, and dry at 105°C before use.~~
- Pre-cleaned Vial - 20 mL capacity, equipped with a screw cap with teflon seal.

4.2 Dohrmann microcoulometric-titration system DX-20A, or equivalent, containing the following components:

- solvent injection system
- pyrolysis furnace
- titration cell

A general description of the analytical system is shown in Figure 1.

4.4 Other Equipment

- Microsyringes - 10 and 25 μL with 26 gauge 4-inch-long needle.
- Laboratory centrifuge to hold 20 mL vials.
- ~~Sonic bath or~~ Sonic probe to fit 20 mL vials. A power level of at least 200 watts is required. ~~or a vortex or for 20 mL vials.~~
- Vials - 2 dram, screw cap with teflon seals
- Metal spatula
- Disposable Pasteur pipettes and bulbs

5.0 Reagents

- Carbon dioxide - gas, 99.9% purity
- Oxygen - 99.9% purity
- Ethyl acetate - Pesticide quality or equivalent
- 1,2,4-Trichlorobenzene - 99%
- 70% Acetic acid in water - Dilute 7 volumes of glacial acetic acid with 3 volumes of water.
- Trichlorobenzene solution, stock (1 μL = 1 μg Cl) - Prepare stock solution by delivering accurately 117 μL (170 mg) of trichlorobenzene into a 100-ML volumetric flask and dilute to volume with ethyl acetate.
- Trichlorobenzene solution, calibration (1 μL = 100 ng Cl) - Dilute 10 mL of the trichlorobenzene stock solution to 100 mL with ethyl acetate.
- Reagent water - Reagent water is defined as a water in which an interferant is not observed at the method detection limit of each parameter of interest (ASTM-1 water).
- Ammonium chloride calibration standard (1 μg Cl^-/μL). Accurately weigh 0.1507 g of ammonium chloride into a 100-mL volumetric flask. Dilute to volume with ASTM-1 water.

6.0 Calibration

6.1 Assemble the solvent injection/pyrolysis/microcoulometric titration apparatus shown in Figure 1 in accordance with the manufacturer's specifications and the modifications shown. The pyrolysis furnace should be set at 840 ± 10°C. Attach the titration cell to the pyrolysis tube outlet and fill the electrolyte (70% acetic acid).

6.2 Turn on the instrument and allow the gas flows and temperatures to stabilize. When the background current of the titration cell has stabilized the instrument is ready for use.

6.3 Calibrate the microcoulometric titration system for Cl^- detection by injecting ~~various amounts of the~~ ammonium chloride calibration standard directly into the titration cell and integrating the response using the POX integration mode. The range of ammonium chloride amounts should cover the range of expected sample concentrations and should always be less than 80 μg Cl^-. Over the range 1 - 80 μg Cl^- the integrated response should read within 2%

or ±0.1 μg (whichever is larger) of the quantity injected. If this calibration requirement is not met then the instrument sensitivity parameters should be adjusted according to the manufacturer's specifications to achieve accurate response.

6.4 Check the performance of the entire analytical system by injecting three 25-μL aliquots of the trichlorobenzene calibrate standard into the furnace at a rate of 5 μl/5 seconds. The mean of these three analyses should be 2.2 - 2.8 μg Cl and the percent relative standard deviation should be 5% or less. If these criteria are not met the system should be checked as described in the instrument maintenance manual in order to isolate the problem.

6.5 Perform a blank ethyl acetate injection (25-μL) each day. If the integrated response is greater than 0.1 μg Cl^-, then the system should be checked for sources of contamination.

Note: If using alternate sample boat technique (described in step 9.6), calibration and ethyl acetate blank volumes may be decreased to as little as 5 μL. Larger sample volumes may overload the system and decrease system performance. Standard recovery shall be between 88-112% and the ethyl acetate blank response shall not exceed 0.1 μg Cl^-.

7.0 Quality Control (QC)

7.1 Each laboratory that uses this method is required to operate a formal QC program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated.

- Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 7.2.

- The laboratory must spike and analyze a minimum of 5% of all samples to monitor continuing laboratory performance and/or each sample matrix shall be spiked to determine recovery.

7.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

- Select a trichlorobenzene spike concentration representative of the expected levels in the samples. Using stock standards, prepare a QC check sample concentrate in ethyl

acetate 100 times more concentrated than the selected concentration.

- Place a minimum of six 1-gram aliquots of an uncontaminated soil sample in 20-mL vials. Spike four of the samples with 10 μL of the check sample, cap the vials, shake vigorously, and allow the spike to equilibrate with the sample by standing overnight. Analyze the aliquots according to the method beginning in Section 9.0.

- Calculate the average percent recovery (R), and the standard deviation of the percent recovery (S), for the results. Soil background corrections must be made before R and S calculations are performed.

- Determine the recovery and single operator precision expected for the method, and compare these results to the values measured and analyzed as described in Section 7.2. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 10.3. [The standard method for setting control limits (SW-846) defines them as R ± 3S. According to the 1,2,4-Trichlorobenzene data in Table I, R = 69% and S = 11%. Combining these, 69 ± 33%, or 36% and 102% would be the lower and upper control limits, respectively.] The laboratory should monitor the frequency of data qualified as suspect to ensure that it remains at or below 5%.

- For non-soil matrices, the six uncontaminated soil samples described in bullet 2 may be replaced with six samples of an alternate matrix. Also, depending on the nature of the alternate sample matrix, the analyst may elect to spike the solvent and immediately extract the sample. Later spiked samples shall be handled and extracted in a fashion consistent with these six QC samples. Spike concentration and method control limits for a given matrix shall be determined as described earlier in this section.

7.3 Each day, the analyst must demonstrate, through the analysis of solvent blank (as described in Section 9), that interferences from the analytical system are under control.

8.0 Sample Collection, Preservation, and Handling

8.1 All samples must be iced or refrigerated from the time of collection until analysis.

8.2 Grab samples must be collected in glass containers having a total volume of at least 25 mL. Fill the sample bottle as completely as possible to minimize head space until time of analysis.

8.3 If the analysis is to be conducted on suspended solids from a waste water sample, isolate the solids by centrifugation, weigh the wet solids, and analyze immediately. ~~Determine the dry weight of a separate portion of the wet solids by heating overnight at 110°C.~~

9.0 Sample Analysis

9.1 Calibrate and check system performance daily as described in Section 6.0.

9.2 Transfer a 1 gram aliquot of the solid sample to a 20 ml vial. Adjust the pH to between 7 and 8 with Sulfuric Acid (H_2SO_4) or Sodium Hydroxide (NaOH). Add anhydrous sodium sulfate at twice the weight of the sample after pH adjustment reagents and mix well. ~~Transfer a 1 gram aliquot of the solid sample to a 20 mL vial using a metal spatula. Add one milliliter of reagent water and five milliliters of ethyl acetate to the sample and cap tightly.~~

9.3 Add 5 ml of Ethyl Acetate and disrupt the sample with a 1/8 inch tapered microtip ultrasonic probe for 2 minutes with a 1 second pulse. Do not exceed the limits for the microtip probe. ~~Shake the sample vigorously for thirty seconds and then place the vial in a sonic bath filled with water to a level of ~1 inch, or agitate the suspension directly using a sonic probe, if available. Sonify the sample for 15 minutes if using a sonic bath or 5 minutes if using a sonic probe or vortex for 15 minutes.~~

9.4 Centrifuge for 15 minutes.

9.5 Transfer the ethyl acetate layer to a clean 2-dram vial, cap, and store refrigerated until analyzed.

9.6 For samples that contain oil or grease contamination or exhibit nonreproducible results, use Section 9.6, bullet 2 and Section 9.7, bullet 2 for an alternate injection method (See Table II).

- For analysis withdraw a 10 to 25-μL aliquot of the ethyl acetate into a microsyringe having a 4-inch long needle. Place the pyrolysis/microcoulometer system into the EOX integration mode and immediately pierce the septum and position the tip of the microsyringe into glass entrance tube. Wait 5 seconds and start the integration cycle. Inject the sample at a rate of approximately 5 μL/5 seconds and withdraw the needle when sample injection is complete.

- For analysis withdraw a 5 to 25 μl aliquot of the ethyl acetate into a microsyringe with needle. With the pyrolysis/microcoulometer system in the TOX integration mode, pierce the septum and inject the sample onto a cerafelt plug in the TOX boat. Withdraw the needle and begin the 12-minute TOX integration cycle. ~~Determine instrument Blank Value with 5 to 25 μl aliquot of the ethyl acetate.~~

9.7

- After the 10-minute integration cycle is complete record the integrated response. If the response exceeds the working range of the instrument repeat the analysis after dilution of the extract with reagent grade ethyl acetate.

- After the integration cycle is complete record the integrated response. If the baseline is not stabilized at this time, depress "Int. Recall" to obtain the total integration since the integration cycle began. If the response exceeds the working range of the instrument repeat the analysis after dilution of the extract with reagent grade ethyl acetate.

10.0 Calculations

10.1 Determine the EOX concentration in the sample as follows:

$$\text{EOX Concentration, } \mu g/g \text{ as } Cl^- = \frac{Q^S \times V_E}{W_S \times V_I} \times 1000$$

where: Q_S = Quantity of EOX as μg of Cl^- in the aliquot injected.
V_I = Volume of aliquot injected in μL.
V_E = Total volume of extract in mL.
W_S = Weight of sample extracted in grams.

10.2 Report results in micrograms per gram. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

10.3 For samples processed as part of a set where the spiked sample recovery falls outside of the control limits which were established according to Section 7.2, data for the affected parameters must be labeled as suspect.

10.4 If the aqueous portion of a water sample, from which the suspended solids are being analyzed, is expected to contain high levels of organic halide, a 1-mL aliquot of the centrifuged sample should be

analyzed. The solids data must then be corrected using the following equation:

$$EOX\ (corrected) = EOX_S - EOX_W \times \frac{W_S}{W_D}$$

where: EOX_S = EOX in wet solids, μg/g as Cl
EOX_W = EOX in water sample, μg/g as Cl
W_S = Wet weight of solids, grams
W_D = Dry weight of solids, grams

11.0 Method Performance

11.1 The method detection limit (MDL) is defined as the minimum concentration of substance that can be measured and reported with 99% confidence that the value is above zero. An MDL of 10 μg/g was obtained using injected ethyl acetate standards. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

11.2 This method is recommended for use in the concentration range from the MDL up to 1000 x MDL.

11.3 In a single laboratory (Battelle Columbus Laboratories), using solid spiked at various levels, the average recoveries presented in Table 1 were obtained.

12.0 References

R. M. Riggin, S. V. Lucas, J. Lathouse, Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater, EPA-600/4-84-008, January 1984. Battelle Columbus Laboratories, 505 King Avenue, Columbus, OH 43201.

USEPA SW-846, 3rd ed. November 1986. Battelle PNL unpublished results.

13.0 Specific Qualification

This process is self-qualifying due to dependence instrument calibration checks with analytical standards and spiked control check samples. (Manual PNL-MA-70, Procedure PAP-70-901, Section 4.2.1).

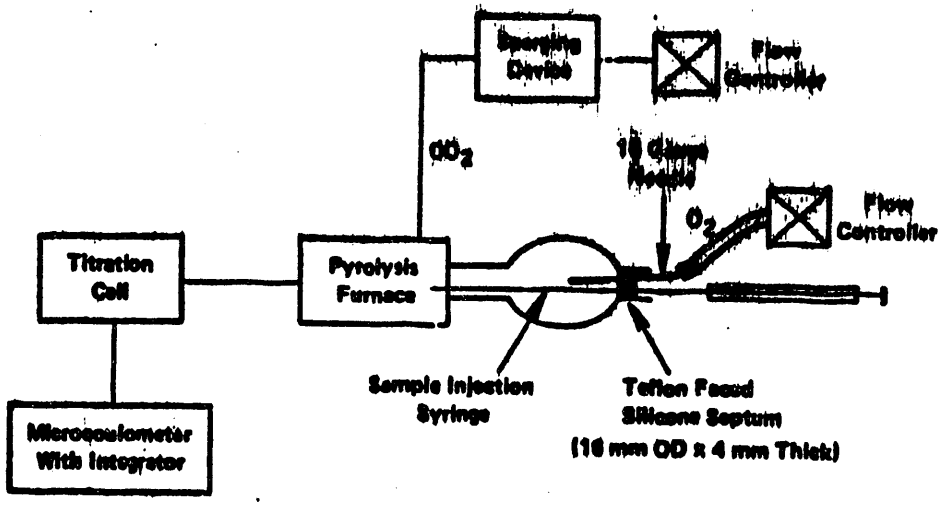

Figure 1. System for determining organic halides in solvent extracts.

TABLE I. EOX METHOD PERFORMANCE DATA FOR VARIOUS SOLID SAMPLES*

Sample	Spike Compound	Spike Level ug/g	Spike Level ug/g as Cl^-	Average Percent Recovery	Standard Deviation of Recovery	Number of Replicates
"Clean Soil"	1,2,4-Trichlorobenzene	10	6	69	11	3
"Clean Soil"	1,2,4-Trichlorobenzene	49	29	103	20	3
"Clean Soil"	2,4,6-Trichloroaniline	47	26	58	15	3
"Clean Soil"	2,4,6-Trichlorophenol	46	25	48	11	3
Suspended Solids from Industrial Effluence	1,2,4-Trichlorobenzene	850	500	104	3	3
Solid Waste from Landfill	1,2,4-Trichlorobenezene	51	30	83	8	3
"Drying Bed" Solid Waste from Chloroethylene Manufacturing	1,2,4-Trichlorobenzene	290	170	94	10	3

* This data was obtained from Battelle Columbus Laboratories

TABLE II: EOX Injection Compared to TOX Boat Injection for Consecutive Sample Introductions of EOX Samples

	Normal EOX Injection				TOX Boat Alternate Injection Method			
Ethyl Acetate Sample*	Result, ng	Avg	Deviation	% Dev.	Result, ng	Avg	Deviation	% Dev.
A	1959				4269			
	2367	2163	408	18.8	4235	4252	34	0.80
B	216							
	483				4464			
	1410	703	1194	170	4525	4994	61	1.22
C	755							
	543							
	775							
	660				4374			
	491	645	284	44.0	4317	4346	57	1.31
D	2394							
	1693							
	1176							
	1873				6174			
	2385	1904	1218	64.0	6077	6136	117	1.91
E	1394				4953			
	1795	1594	401	25.2	5054	5004	101	2.02

* This data was obtained from Battelle PNL.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-321, TOTAL ORGANIC HALIDES FOR LIQUID SAMPLES

APPLICABILITY

This procedure applies to the determination of total organic halides (TOX) in liquid samples. The results are reported as chloride, although bromine and iodine are measured. Compounds containing fluorine are not determined by this procedure. The procedure involves adsorption of the compound on a carbon column, column wash to remove trapped inorganic halides, and conversion of the adsorbed organohalide to the ionic halide which can be titrated by microcoulometry.

DEFINITIONS

None

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

PROCEDURE

See Attachment 1 for the detailed procedure.

QUALITY CONTROL

See Section 8.0 in Attachment 1.

REFERENCES

TOTAL ORGANIC HALIDES (TOX), SW-846, Method 9020, Test Methods for Evaluating Solid Waste, Third Edition, United States Environmental Protection Agency, November 1986.

Author	Date	Project Mgr.	Date	QAD Representative	Date
[signature]	12/12/89	[signature]	12/13/89	[signature]	12-13-89
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
[signature]	10-26-89	[signature]	12/13/89		

Procedure No.	Revision No.	Effective Date	Page	of
PNL-ALO-321	0	DEC 13 1989	1	1

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METHOD 9020

TOTAL ORGANIC HALIDES (TOX)

1.0 Scope and Application

1.1 Method 9020 determines Total Organic Halides (TOX) as Cl^- in drinking and ground waters. The method uses carbon adsorption with a microcoulometric-titration detector. It requires that all samples be run in duplicate. Under conditions of duplicate analysis, the reliable limit of sensitivity is 5 µg/l.

1.2 Method 9020 detects all organic halides containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine-containing species are not determined by this method.

1.3 Method 9020 is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

1.4 Method 9020 is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcoulometer and in the interpretation of the results.

1.5 This method is provided as a recommended procedure. It may be used as a reference for comparing the suitability of other methods thought to be appropriate for measurement of TOX (i.e., by comparison of sensitivity, accuracy, and precision data).

2.0 Summary of Method

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and that is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed to remove any trapped inorganic halides, and is then analyzed to convert the adsorbed organohalides to a titratable species that can be measured by a microcoulometric detector.

3.0 Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be

routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400° C for 15 to 30 min. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases helps to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples that register less than 1000 ng/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two-week supply should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

4.0 Apparatus and Materials

4.1 Adsorption system

4.1.1 Dohrmann adsorption module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

4.1.2 Adsorption columns: Pyrex, 5-cm-long x 6-mm-O.D. x 2-mm-I.D.

4.2.3 Granular activated carbon (GAC): Filtrasorb-400, Calgon-APC or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent-halide background should be 1000 mg Cl^- equivalent or less.

4.1.4 Cerafelt (available from Johns-Manville), or equivalent: Form this material into plugs using a 2-mm-I.D. stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. CAUTION: Do not touch this material with your fingers.

4.1.5 Column holders (available from Dohrmann).

4.1.6 Volumetric flasks: 100-ml, 50-ml. A general schematic of the adsorption system is shown in Figure 1.

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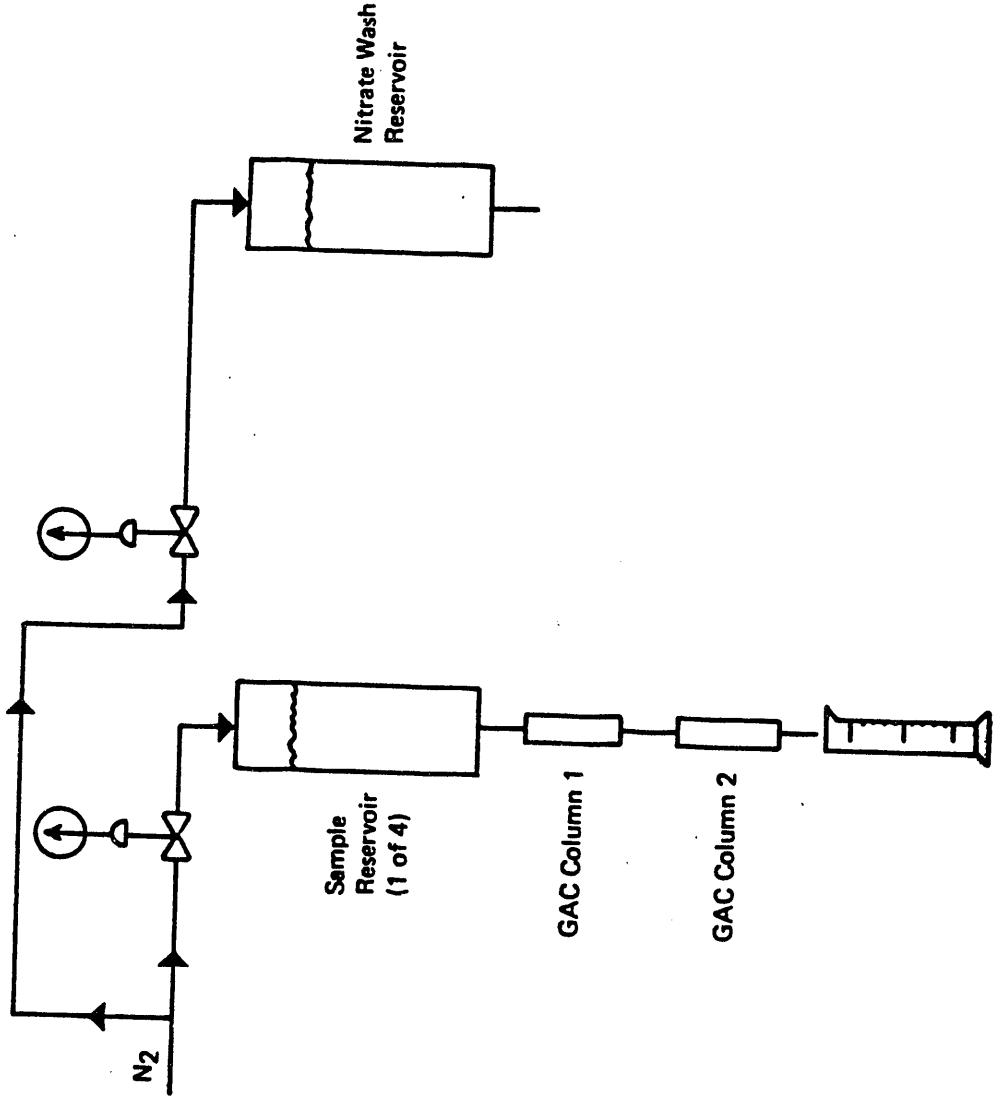

Figure 1. Schematic of Adsorption System.

4.2 Dohrmann microcoulometric-titration system (MCTS-20 or DX-20), or equivalent, containing the following components:

4.2.1 Boat sampler.

4.2.2 Pyrolysis furnace.

4.2.3 Microcoulometer with integrator.

4.2.4 Titration cell: A general description of the analytical system is shown in Figure 2.

4.3 Strip chart recorder.

5.0 Reagents

5.1 Sodium sulfite: 0.1 M, ACS reagent grade (12.6 g/liter).

5.2 Nitric acid: Concentrated.

5.3 Nitrate-wash solution (5000 mg NO_3^-/l): Prepare a nitrate-wash solution by transferring approximately 8.2 g of potassium nitrate into a 1-liter volumetric flask and diluting to volume with reagent water.

5.4 Carbon dioxide: Gas, 99.9% purity.

5.5 Oxygen: 99.9% purity.

5.6 Nitrogen: Prepurified.

5.7 70% acetic acid in water: Dilute 7 volumes of acetic acid with 3 volumes of water.

5.8 Trichlorophenol solution, stock (1 µl = 10 µg Cl^-): Prepare a stock solution by weighing accurately 1.856 g of trichlorophenol into a 100-ml volumetric flask. Dilute to volume with methanol.

5.9 Trichlorophenol solution, calibration (1 µl = 500 ng Cl^-): Dilute 5 ml of the trichlorophenol stock solution to 100 ml with methanol.

5.10 Trichlorophenol standard, instrument-calibration: First, nitrate-wash a single column packed with 40 mg of activated carbon as instructed for sample analysis, and then inject the column with 10 µl of the calibration solution.

5.11 Trichlorophenol standard, adsorption-efficiency (100 µg Cl^-/liter): Prepare an adsorption-efficiency standard by injecting 10 µl of stock solution into 1 liter of reagent water.

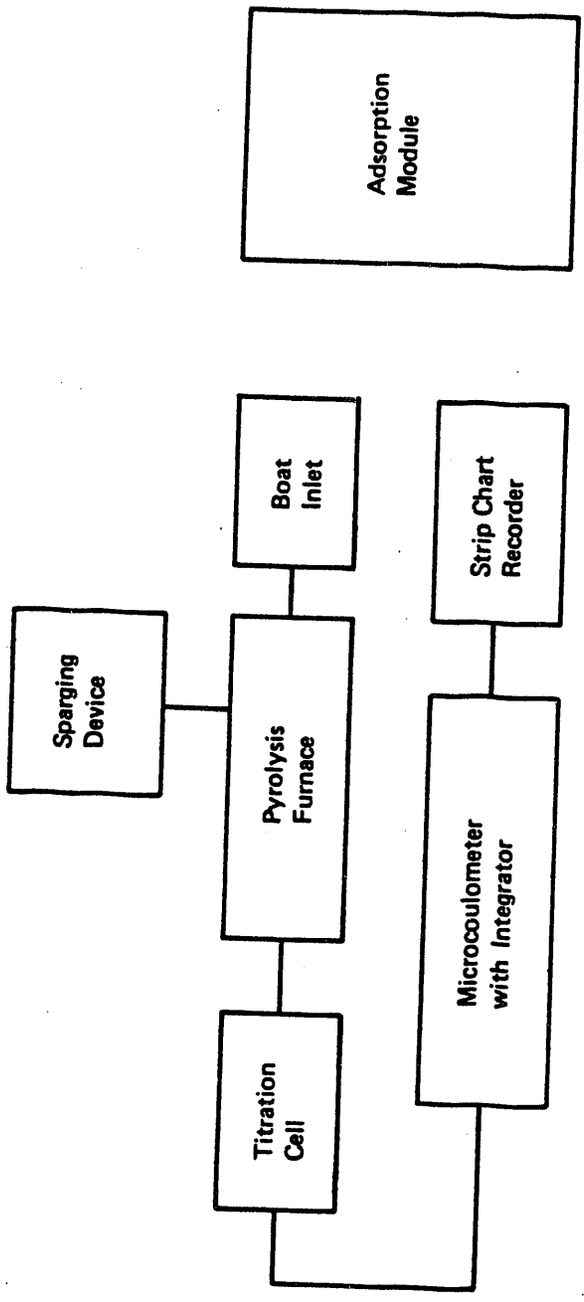

Figure 2. Schematic diagram of CAOX analysis system.

5.12 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

5.13 Blank standard: The reagent water used to prepare the calibration standard should be used as the blank standard.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All samples should be collected in bottles with teflon septa (e.g., Pierce #12722 or equivalent) and be protected from light. If this is not possible, use amber glass, 250-ml, fitted with teflon-lined caps. Foil may be substituted for teflon if the sample is not corrosive. Samples must be protected against loss of volatiles by eliminating headspace in the container. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400° C before use, to minimize contamination.

6.3 All glassware must be dried prior to use according to the method discussed in 3.1.1.

7.0 Procedure

7.1 Sample preparation

7.1.1 Special care should be taken in handling the sample in order to minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

7.1.2 Reduce residual chlorine by adding sulfite (1 ml of 0.1 M per liter of sample). Sulfite should be added at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at 4° C without headspace.

7.1.3 Adjust the pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the reservoir.

7.2 Calibration

7.2.1 Check the adsorption efficiency of each newly-prepared batch of carbon by analyzing 100 ml of the adsorption-efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2.2 Nitrate-wash blanks (method blanks): Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight pyrolysis determinations. The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution as instructed for sample analysis, and then pyrolyze the carbon.

7.2.3 Pyrolyze duplicate instrument-calibration standards and the blank standard each day before beginning sample analysis. The net response to the calibration-standard should be within 3% of the calibration-standard value. Repeat analysis of the instrument-calibration standard after each group of eight pyrolysis determinations, and before resuming sample analysis after cleaning or reconditioning the titration cell or pyrolysis system.

7.3 Adsorption procedure

7.3.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

7.3.2 Fill the sample reservoir, and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 ml/min. NOTE: 100 ml of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/l; 50 ml for 501 to 1000 µg/l, and 25 ml for 1001 to 2000 µg/l.

7.3.3 Wash the columns-in-series with 2 ml of the 5000-mg/l nitrate solution at a rate of approximately 2 ml/min to displace inorganic chloride ions.

7.4 Pyrolysis procedure

7.4.1 The contents of each column are pyrolyzed separately. After rinsing with the nitrate solution, the columns should be protected from the atmosphere and other sources of contamination until ready for further analysis.

7.4.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a CO_2-rich atmosphere at a low temperature to ensure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an O_2-rich atmosphere. NOTE: The quartz sampling boat should have been previously muffled at 800° C for at least 2 to 4 min as in a previous analysis, and should be cleaned of any residue by vacuuming.

7.4.3 Transfer the contents of each column to the quartz boat for individual analysis.

7.4.4 If the Dohrmann MC-1 is used for pyrolysis, manual instructions are followed for gas flow regulation. If the MCTS-20 is used, the information on the diagram in Figure 3 is used for gas flow regulation.

7.4.5 Position the sample for 2 min in the 200° C zone of the pyrolysis tube. For the MCTS-20, the boat is positioned just outside the furnace entrance.

7.4.6 After 2 min, advance the boat into the 800° C zone (center) of the pyrolysis furnace. This second and final stage of pyrolysis may require from 6 to 10 min to complete.

7.5 Detection: The effluent gases are directly analyzed in the micro-coulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

7.6 Breakthrough. The unpredictable nature of the background bias makes it especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-column measurements for a properly operating system should not exceed 10% of the two-column total measurement. If the 10% figure is exceeded, one of three events can be happening. Either (1) the first column was overloaded and a legitimate measure of breakthrough was obtained, in which case taking a smaller sample may be necessary; or (2) channeling or some other failure occurred, in which case the sample may need to be rerun; or (3) a high random bias occurred and the result should be rejected and the sample rerun. Because it may not be possible to determine which event occurred, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analysis that is rejected should be repeated whenever sample is available. If the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

7.7 Calculations: TOX as Cl^- is calculated using the following formula:

$$\frac{(C_1-C_3) + (C_2 - C_3)}{V} = \mu g/l \text{ Total Organic Halide}$$

where:

C_1 = µg Cl^- on the first column in series

C_2 = µg Cl^- on the second column in series

C_3 = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column)

V = the sample volume in liters.

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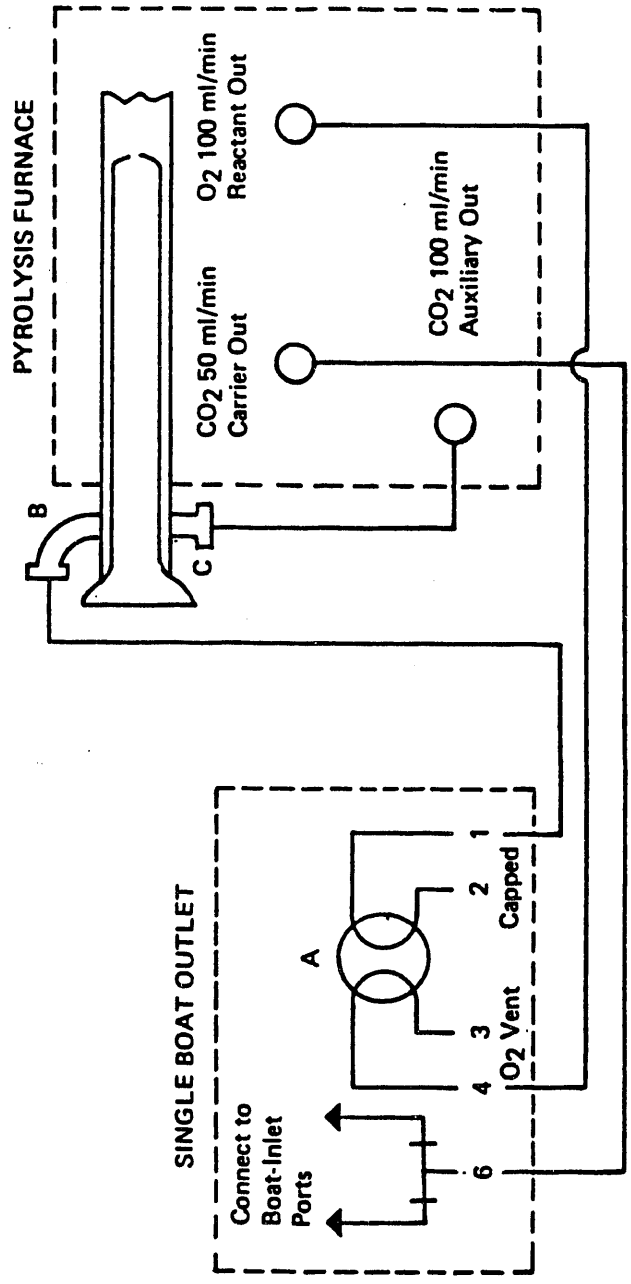

Figure 3. Rear-view plumbing schematic for MCTS–20 System. Valve A is set for first-stage combustion, O_2 venting (push/pull valve out). Port B enters inner combustion tube; Port C enters outer combustion tube.

10 / MISCELLANEOUS ANALYTICAL METHODS

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by analyzing appropriate quality-control check samples.

8.3 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Run check standard after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparations process.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-322, Analysis by Gas Chromatography/Fourier Transform-Infrared Spectroscopy

APPLICABILITY

QUALITATIVE ANALYSIS:

The use of gas chromatography/fourier transform-infrared spectroscopy (GC/FTIR) provides information to the analyst regarding the functional groups associated with organic molecules. It is complementary to the gas chromatograph-mass spectrometer system. Samples such as soil, water, and sludges may be prepared according to an established procedure (for example PNL-ALO-335). These extracted sample residues can be analyzed directly or diluted prior to running on the GC/FTIR. The resulting retention time and IR spectra generated can serve as the sole identifier for fairly simple molecules. However, IR spectral interpretation seldom yields a complete molecular structure of more complex organic arrangements. It is nonetheless a very powerful technique for obtaining valuable clues about the identity of an unknown, particularly when combined with mass spectral data.

QUANTITATIVE ANALYSIS:

GC/Fourier Transform Infrared spectrophotometry can also be used for quantitative analysis. The amount of radiation absorbed at a given wavelength is dependent upon concentration as well as its molecular composition. Sensitivity for any particular compound is highly dependent upon the functional groups present and their ability to absorb or re-transmit in the infrared frequency range.

SYSTEM DESCRIPTION:

The extracted sample residue is injected onto a chromatographic column and the analytes contained in the sample are separated based upon various parameters such as their affinity to the GC column and the system temperature. The end of the GC column extends through a heated interface and to the IR flow cell. As each component elutes from the GC column, it passes through the flow cell. The spectrophotometer measures, repeatedly and as fast as possible, the infrared spectrum of the flow cell contents.

Author	Date	Project Mgr.	Date	QAD Representative	Date
E.W. Hoppe	10-14-91	B.M. Gillespie	9-25-91	G.K. Gerke for GKG.	10/16/91
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
R.W. Stromatt	10-16-91	A.G. King	10-17-91		

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When only carrier gas is present, there is no detectable absorption. When a compound elutes, absorbance/transmittance data is obtained. This absorbance/transmittance pattern is monitored by the detector which converts the light intensity signal to an electrical signal. A characteristic absorbance or transmittance spectrum, as well as a chromatogram, is then displayed and recorded by the computer system. The pattern obtained depends on the identity of the compound and the amount of radiation absorbed depends on the quantity of compound present. The IR technique is non-destructive so the effluent from the flow cell may be connected to other detectors of choice such as an FID, MS, etc.

DEFINITIONS

GC/FTIR - Gas chromatograph/fourier transform infrared spectrometry
GC/MS - Gas chromatograph/mass spectrometry

RESPONSIBLE STAFF

Cognizant Scientist
Analyst

PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 This method may be used as an aid in the determination of an unknown sample's constituents. It may also be used for determining relative quantities of tentatively identified compounds using response factors of known compounds. Quantitative determinations may be made when standards of target compounds are obtained and the system is calibrated prior to analysis of samples.

2.0 SUMMARY OF METHOD

2.1 A daily "dry" analysis is performed to ascertain the detector background. Then, the appropriate system performance standard is injected to assess operation of the GC/FTIR system. An aliquot of sample extract is injected into the GC/FTIR. The spectra obtained are compared to library or pre-run reference spectra and reviewed by the analyst for compound or functional group determination. Quantitation is performed when a multi-point calibration of the appropriate standard is run prior to sample analysis.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, and glassware. All these materials shall be routinely demonstrated to be free from contaminants through the analysis of method blanks.

3.2 The infrared detector varies considerably in sensitivity for various compounds. It is highly recommended that the IR detector effluent is monitored with a more sensitive and consistent detector. For example, a flame ionization detector is suitable for general monitoring purposes.

4.0 APPARATUS AND MATERIALS

4.1 Reagents

4.1.1 Various "GC grade" or "Pesticide Residue grade" solvents are suitable as needed for the dilution of residues or standards. Methylene Chloride and hexane are examples.

4.1.2 System Performance Assessment Standards: These are standards that contain compounds of similar boiling point and polarity to those anticipated to be of interest in the sample. They are used to qualitatively evaluate the system performance. For example, appropriate standards for system performance assessment may be the internal standards mix for volatile analysis (see method PNL-ALO-335) or semi-volatile analysis (see method PNL-ALO-345). The semi-volatile internal standard mix may be employed when evaluating a residue for unknown compounds of a similar boiling point (semi-volatile range) and polarity range.

4.1.3 Quantitative Analysis Standards: These are standards that shall be used whenever quantitation of known analytes is performed. They may be obtained from vendors as certified neat materials, stock, or standard solutions.

4.2 Equipment and Materials

4.2.1 GC/FTIR Hewlett-Packard system comprised of a model HP5965A IR detector, an HP5890 II gas chromatograph, and the HP59970 IRD chemstation including manufacturer specified supporting hardware and software

4.2.2 High purity gases: Helium, Nitrogen.

4.2.3 Gas-tight syringes: 10.0 ul size for injections, and up to 1000 ul as needed for dilutions. Manufacturer specified accuracy and repeatability to within +/- 1%.

4.2.4 1 mL amber sample vials with teflon lined screw cap or crimp-on style cap.

4.2.5 Liquid nitrogen.

5.0 ANALYSIS

5.1 System Start-up

5.1.1 The system is turned on and liquid nitrogen added to the detector. The system is allowed to stabilize for at least one hour according to the manufacturer's specifications.

5.1.2 Align the optics and perform a mirror calibration as necessary according to the manufacturer instructions.

5.1.3 A "dry" run consisting of a 1-2 ul injection of the appropriate solvent or no injection at all is performed. The intent is for the system to thermally cycle through the temperature program. This will allow any residual background water or other contamination to elute from the system.

5.1.4 The system background response is evaluated prior to sample analysis. If the background during the "dry" run is higher than the manufacturer's recommendations or unsuitable for some other reason, corrective action as defined by the cognizant scientist or the instrument operating manual shall be performed prior to running samples.

5.1.5 Using a 10.0 ul gas tight syringe, inject 1-2 ul of the appropriate system performance standard. The system is evaluated by the scientist for adequate response, peak shape, retention time behavior and spectral integrity using GC/MS internal standard mixes or some other suitable standard specified by the cognizant scientist. In addition, this standard provides response factors which can be used to qualitatively determine relative amounts of tentatively identified compounds if this is desired.

5.1.6 Gas chromatographic conditions are varied as necessary to achieve optimal analyte separation. Changes are made with the concurrence of the cognizant scientist and are documented in the lab record or LRB.

5.1.7 If a quantitative determination of known target analytes is to be performed, then a multi-point calibration at a minimum of three concentrations levels shall be performed. Sample injections shall be made using the

same injection volume as the system performance standard and the multi-point calibration. Document the calibration concentration levels and solutions used.

5.1.8 Since no calibration performance criteria have been established, quantitation shall only be made when the response of the sample is bracketed by the response from the calibration standards. Quantitation may be performed by using the average relative response factor or a linear best-fit as determined by the cognizant scientist. Methods may be developed which include more specific calibration performance criteria.

5.1.9 Spectra obtained from a GC run are reviewed by the cognizant scientist. Where possible, molecular identifications are made or functional groups are determined. The data system provides matching of the IR spectral libraries and functional group information.

6.0 QUALITY CONTROL

6.1 Prior to analysis of samples for the day, an evaluation of the system background shall be performed. Several blank or "dry" runs may need to be made to lower a substantial background to the manufacturer's recommended levels.

6.2 The system performance standard (internal standard or other suitable standard as determined by the cognizant scientist) shall be run at least daily to assess detector response, peak shape, retention time, and spectra characteristics.

6.3 Method blanks, which have been taken through the entire appropriate extraction process, shall be analyzed to assure that the sample residues are free from laboratory introduced contamination.

6.4 Tolerances for all values given in this method are to within the first, non-zero, significant figure. The significant integer shall include the number 10. For example, 5 mL implies an accuracy to within +/- 1 mL, while 5.0 mL implies accuracy to within +/- 0.1 mL. If 1000 mL is specified, it implies an accuracy to +/- 100 mL because the first significant figure is 10.

7.0 METHOD PERFORMANCE AND SPECIFIC QUALIFICATION

7.1 This method is self qualifying due to dependence on certified analytical standards if quantitation is performed. It uses well established library reference spectra for compound or functional group identifications. It is qualified additionally through independent technical review.

REFERENCES

1. System Handbook, HP 5965B Infrared Detector and HP 59970C IRD Chemstation, Publication No. 05965-90032, January 1990.

2. GC/MS Analysis of Volatile Organic Compounds, PNL-ALO-335, rev. 0, August 3, 1989.

3. GC/MS Analysis of Extractable Semi-volatile Organic Compounds, PNL-ALO-345, rev. 0, August 3, 1989.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-330, SCREENING OF HEXADECANE EXTRACTS FOR VOLATILE ORGANIC COMPOUNDS

APPLICABILITY

This procedure applies to the gas chromatograph/flame ionization detector (GC/FID) screening analysis of hexadecane extracts of water and solid material samples. The purpose of the screen is to determine conditions for the sample preparation for the gas chromatograph/mass spectrometry (GC/MS) measurement of volatile organic compounds, PNL-ALO-335.

DEFINITIONS

None

RESPONSIBLE STAFF

Cognizant Staff
Analyst

PROCEDURE

1.0 Scope and Application

1.1 This method is a screening procedure for use with purge-and-trap GC or GC/MS. The results of this analysis are purely qualitative and should not be used as an alternative to more detailed and accurate quantitation methods.

2.0 Summary of Method

2.1 An aliquot of sample is extracted with hexadecane and then analyzed by GC/FID. The results of this analysis will indicate whether the sample requires dilution or methanolic extraction prior to purge-and-trap GC or GC/MS analysis. Effluent from detection must be vented into a hood suitable for radioactive use.

3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, and glassware. All these materials must be routinely

Author	Date	Project Mgr.	Date	QAD Representative	Date
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Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
[signature]	5/23/90	[signature]	5/23/90	N/A	

demonstrated to be free from contaminants by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of interferences will vary considerably from sample to sample depending upon the nature and diversity of the matrix being sampled.

3.2 The flame ionization detector varies considerably in sensitivity when comparing aromatics and halogenated methanes and ethanes. Halomethanes are approximately 1/20 as sensitive as aromatics and haloethanes approximately 1/10 as sensitive. Low-molecular-weight, water-soluble solvents (e.g., alcohols and ketones) will extract poorly from the water, and therefore will exhibit low sensitivity on the GC/FID.

4.0 Apparatus and Materials

4.1 Balance: Analytical, Capable of accurately weighing 0.0001 gm.

4.2 Gas Chromatograph: An analytical system complete with gas chromatograph suitable for on-column or packed column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder (or equivalent). A data system is highly recommended for measuring peak heights and/or peak areas.

4.2.1 Detector: Flame ionization (FID).

4.2.2 GC Column: Any column capable of resolving the majority of target volatile compounds may be used. A megabore (0.53mm diameter) DB-5 column, 30 meters in length with a 1.5 micron film thickness has proven to perform well. A flow rate of ~8mL/min at 40°C using helium as a carrier gas and a packed column injector at 275°C was used. The column temperature was programmed from an initial temperature of 40° for 5.0 minutes, increased to 100° at 6°/min, held at 100° for 1.0 minutes, then increased to 280° at 60°/min, held at 280° for 20 minutes.

Other suggested columns are: DB624 (megabore), DB-1 (megabore and capillary), DB-5 (capillary), 10% OV-101 (packed glass).

4.3 Centrifuge: Capable of accommodating 16mm glass screw top culture tubes.

4.4 Vials and caps: 2-mL for GC autosampler.

4.5 Volumetric flasks; 10- and 50-mL with ground-glass stopper or Teflon-lined screw-cap.

4.6 Culture tubes: ~15-mL with Teflon-lined screw-cap, 16mm diameter.

4.7 Pasteur pipits: Disposable.

4.8 Bottles: 20-mL pre-cleaned vials (I-chem or equivalent), 0.125" Teflon-lined silicone septa.

5.0 Reagents

5.1 Hexadecane and methanol: Pesticide quality or equivalent.

5.2 Reagent water: Reagent water is defined as water in which an interference is not observed at the method detection limit of each parameter of interest.

5.3 Stock standard solutions: (1.00 ug/uL): Stock standard solutions can be purchased as certified solutions or can be prepared from pure standard materials.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams of pure material. Dissolve the material in methanol in a 10-mL volumetric flask and dilute to volume (larger volumes may be used at the convenience of the analyst). If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially available stock standards may be used if they are certified by the manufacturer.

5.3.2 Transfer the stock standards into appropriately sized Teflon-sealed screw-cap bottles, minimize the headspace above the solution.

5.4 Working standard solution (100ng/μL): Prepare a working standard (through dilution of stock standard solutions) containing benzene, toluene, ethyl benzene, xylenes (m,o,p), n-nonane, and n-dodecane in which the concentration of each compound in the solution is 100 ng/μL in methanol. Store at 4°C or less and protect from light. These standards should be checked occasionally for signs of degradation or evaporation. Discard these no more than 1 year from preparation.

6.0 Sample Collection, Preservation, and Handling

6.1 Samples for volatile analysis should fill the sampling vial as completely as possible to minimize headspace above the sample. The sample vials should then be stored at 4°C and protected from light. Analysis should occur within 14 days, although screening is usually performed earlier to allow to provide data in time for subsequent GC/MS analysis.

7.0 Procedure

7.1 Sample preparation: The following sample and reagent amounts may be modified. Care should be taken to keep track of the modifications effect on the final dilution factor used for quantitative analysis.

7.1.1 Water:

7.1.1.1 Allow the contents of the sample vial to come to room temperature. If the sample is not in a 20-mL vial, quickly transfer 4 mLs into a 20-mL vial. Immediately add 2.0 mL of hexadecane, cap the vial, and shake the contents vigorously for 1 min. Let the phases separate.

7.1.1.2 Transfer approximately 1 mL of the hexadecane layer to a 2.0-mL GC vial and cap. If an emulsion is present after shaking the sample, break it by:

1. pulling the emulsion through a small plug of Pyrex glass wool packed in a pipet, or

2. transferring the emulsion to a culture tube and centrifuging for several min.

7.1.2 Standards:

7.1.2.1 Add 20 uL of the working standard mixture to 4-mL portions of reagent water. Follow the instructions in Sections 7.1.1.1 and 7.1.1.2 with the immediate addition of 2.0 mL of hexadecane.

7.1.3 Sediment/Soil/Sludge:

7.1.3.1 To approximately 1 g of sample (wet weight) contained in a 20 ml vial, add 4-mL of reagent water. Cap and shake vigorously for 1 min.

7.1.3.2 Follow the instructions given in Section 7.1.1.1 and 7.1.1.2, starting with the addition of 2.0 mL of hexadecane.

7.1.4 Spikes:

Immediately prior to performing the extraction procedure, add 20 μL of the working standard solution to an aliquot of the sample. Follow the instructions given for extraction of the appropriate matrix, adequate sample permitting.

7.2 Analysis:

7.2.1 Calibration:

7.2.1.1 External standard calibration: The GC/FID must be calibrated each 12-hour shift for half of full-scale response when injecting 1 uL of the extracted standard mixture (co-eluting xylene isomers may result in greater than half scale response).

7.2.2 GC/FID analysis: Inject the same volume of hexadecane extract for the sample under investigation as was used to perform the external standard calibration. The GC conditions used for the standards analysis must also be the same as those used to analyze the samples.

7.2.3 Interpretation of the GC/FID chromatograms: Compare the hexadecane sample extract chromatograms against an extracted standard chromatogram.

7.2.3.1 If no peaks prior to the elution of hexadecane are noted on the sample chromatogram, the sample can be analyzed using the low level purge and trap procedure.

7.2.3.2 If peaks are present, use the following formula to determine the dilution factor(X):

$$X(\text{dilution factor}) = \frac{\text{area of major peak in sample}}{\text{area of nearest standard peak}} + 1$$

7.2.3.3 It is not recommended that n-dodecane is used as the standard peak unless it is completely resolved and elutes on a flat baseline prior to hexadecane. Using the area for n-nonane for late eluting peaks is less difficult. Use the information provided in Table 1 to determine how the sample should be handled for GC/MS analysis.

7.2.3.4 If a high-level method is indicated, the information provided in Table 2 can be used to determine the volume of methanol extract to add to 5 mL of reagent water for analysis.

8.0 Quality Control

8.1 It is recommended that a reagent blank be analyzed by this screening procedure to ensure that no laboratory contamination exists. A blank should be performed for each set of samples undergoing extraction and screening.

9.0 Method Performance and Specific Qualification

9.1 This procedure is self-qualifying due to dependence on analytical standards and to routinely demonstrate a signal to noise exceeding 20:1. It is qualified additionally through quality control samples and by Independent Technical Review.

REFERENCES

1. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, February 1988, Revision.

2. U.S. EPA Test Methods for Evaluating Solid Waste, Vol. IB, SW-846, 3rd Edition, November 1986.

TABLE 1: Determination of GC/MS Purge-and-Trap Method

X Factor	Approximate Concentration Range[a]	Analyze by
0-1.0	0-1,000 ug/kg	Low-level method
>1.0	>1,000 ug/kg	High-level method

[a] This concentration range is based upon the response of aromatics to GC/FID. The concentration for halomethanes is 20x higher, and haloethanes 10x higher, when comparing GC/FID responses.

TABLE 2: Quantity of Methanol Extract Required for Analysis of High-Level Soil/Sediments

X Factor	Approximate Concentration Range[a]	Volume of Methanol Extract[b]
0.25-5.0	500-10,000 ug/kg	100 ul
0.5-10.0	1,000-20,000 ug/kg	50 ul
2.5-50.0	5,000-100,000 ug/kg	10 ul
12.5-250	25,000-500,000 ug/kg	100 ul of 1/50 dilution[c]

[a] Actual concentration ranges could be 10 to 20 times higher than this if the compounds are halogenated and the estimates are from GC/FID.

[b] The volume of methanol added to 5 mL of water being purged should be 100 uL. Therefore if the amount of methanol extract required is less than 100 uL, additional methanol should be added to maintain the constant 100 uL volume.

[c] Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-331, SCREENING OF HEADSPACE EXTRACTS FOR VOLATILE ORGANIC COMPOUNDS

APPLICABILITY

This procedure is a modification of Method 3810 from SW-846 and applies to the gas chromatographic/flame ionization detector screening analysis of static headspace extracted volatile organic compounds in liquid and solid samples. The purpose of the screen is to assist in sample size selection for the GC/MS Analysis for Volatile Organic Compounds, PNL-ALO-335.

DEFINITIONS

None

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 This method is a static headspace technique for extracting volatile organic compounds from samples. It is a simple method that allows large numbers of samples to be screened in a relatively short period of time. It is ideal for screening samples prior to using the purge-and trap method. Detection limits for this method may vary widely among samples because of the large variability and complicated matrices of waste samples. The method works best for compounds with boiling points of less than 125°C. The sensitivity of this method will depend on the equilibria of the various compounds between the vapor and dissolved phases.

1.2 Due to the variability of this method, this procedure is recommended for use only as a screening procedure for other, more accurate determinative methods (Methods 8010, 8015, 8020, 8030, 8240 and PNL-ALO-335).

Author	Date	Project Mgr.	Date	QAD Representative	Date
[signature]	5-4-90	[signature]	5/15/90	[signature]	5/21/90
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
[signature]	5-18-90	[signature]	5/18/90	N/A	

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2.0 SUMMARY OF METHOD

2.1 The sample is collected in sealed glass containers and allowed to equilibrate at 90°C. A sample of the headspace gas is withdrawn with a gastight syringe for screening analysis using the conditions specified in one of the GC or GC/MS determinative methods (8010, 8015, 8020, 8030, 8240 and PNL-ALO-335). Effluent from detectors must be vented into a hood suitable for radioactive use.

3.0 INTERFERENCES

3.1 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water. It may be necessary to wash out the syringe with detergent, rinse with distilled water, and dry in a 105°C oven between analyses.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free.

4.0 APPARATUS AND MATERIALS

4.1 Balance: Analytical, capable of accurately weighing 0.0001 gm.

4.2 Vials: 20-mL Hypo-Vials (Pierce Chemical Co., #12995, or equivalent), four each, with screw tops.

4.3 Septa: Tuf-Bond (Pierce #12720 or equivalent), 0.125" thickness.

4.4 Microsyringe: 250- or 500-uL.

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control (±3°C). The bath should be used in a hood.

4.6 Gas Chromatograph: An analytical system complete with gas chromatograph suitable for on-column or packed column injection and all required accessories including syringes, analytical columns,

gases, detector, and strip-chart recorder (or equivalent). A data system is highly recommended for measuring peak heights and/or peak areas.

4.6.1 Detector: Flame ionization (FID).

4.6.2 GC column: Any column capable of resolving the majority of target volatile compounds may be used. A megabore (0.53mm diameter) DB-5 column, 30 meters in length with a 1.5 micron film thickness has proven to perform well. A flow rate of ~8 ml/min at 40°C using helium as a carrier gas and a packed column injector at 275° was used. The column temperature was programmed from an initial temperature of 40° for 5.0 minutes, increased to 100° at 6°/min, held at 100° for 1.0 minutes, then increased to 280° at 60°/min, held at 280° for 20 minutes.

Other suggested columns are: DB624 (megabore), DB-1 (megabore and capillary), DB5 (capillary), 10% OV-101 (packed glass).

5.0 REAGENTS

5.1 Methanol: Pesticide quality or equivalent.

5.2 Reagent water: Reagent water is defined as water in which an interference is not observed at the method detection limit of each parameter of interest.

5.3 Stock standard solutions (1.00 ug/uL): Stock standard solutions can be purchased as certified solutions or can be prepared from pure standard materials.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams of pure material. Dissolve the material in methanol in a 10-mL volumetric flask and dilute to volume (larger volumes may be used at the convenience of the analyst). If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially available stock standards may be used if they are certified by the manufacturer.

5.3.2 Transfer the stock standards into appropriately sized Teflon-sealed screw-cap bottles, minimize the headspace above the solution. Store at 4°C and protect from light.

These standards should be checked occasionally for signs of degradation or evaporation.

5.4 Working Standard Solution (100ng/μL): Prepare a working standard (through dilution of Stock Standard Solutions) containing benzene, toluene, ethyl benzene, xylenes (m,o,p), n-nonane, and n-dodecane in which the concentration of each compound in the solution is 100 ng/μL in methanol.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples for volatile analysis should fill the sampling vial a completely as possible to minimize headspace above the sample. The sample vials should then be stored at 4°C and protected from light. Analysis should occur within 14 days, although screening is usually performed earlier to allow time for subsequent GC/MS analysis.

7.0 PROCEDURE

7.1 The following sample and reagent amounts may be modified. Care should be taken to keep track of the modifications effect on the final dilution factor used for quantitative analysis.

7.2 Sample preparation:

7.2.1 Place 1.0 g of a well-mixed waste sample into each of two separate 20-mL septum-seal vials.

7.2.2 Adequate sample permitting, spike one sample vial through the septum with 20 uL of a 100 ng/uL calibration standard containing the compounds of interest. Label this "2-ppm spike."

7.2.3 Dose a separate (empty) 20-mL septum seal vial with 20 uL of the same 100 ng/uL calibration standard. Label this "2-ppm standard."

7.2.4 Place the sample, 2-ppm-spike, 2-ppm-standard, and an empty "blank" vial into a 90°C water bath for 1 hr. Store any remaining sample vials at 4.0°C for possible future analysis.

7.3 Sample analysis

7.3.1 While maintaining the vials at 90°C, withdraw 250 uL of the headspace gas with a warm gas-tight syringe and analyze by direct injection into a GC.

7.3.2 Analyze the 2-ppm standard and adjust instrument sensitivity to give a minimum response of approximately one-half scale. Record retention times (RT) and peak areas of compounds of interest. (co-eluting xylene isomers may result in greater than half scale responses).

7.3.3 Analyze the "blank" vial.

7.3.4 Analyze the 2-ppm spiked sample in the same manner. Record RTs and peak areas.

7.3.5 Analyze the unspiked sample as in Paragraph 7.3.4.

7.3.6 Use the results obtained to determine if the sample requires dilution or methanolic extraction as follows:

7.3.6.1 Compare the sample extract chromatograms against an extracted standard chromatogram.

7.3.6.2 If no peaks are noted on the sample chromatogram, the sample can be analyzed using the low-level purge and trap procedure.

7.3.6.3 If peaks are present, use the following formula to determine the dilution factor (X):

$$X(\text{dilution factor}) = \frac{\text{area of major peak in sample}}{\text{area of nearest standard peak}} + 1$$

7.3.6.4 It is not recommended that n-dodecane is used as the standard peak unless it is completely resolved and elutes on a flat baseline. Using the area for n-nonane for late eluting peaks is less difficult. Use the information provided in Table 1 to determine how the sample should be handled for GC/MS analysis.

7.3.6.5 If a high-level method is indicated, the information provided in Table 2 can be used to determine the volume of methanol extract to add to 5 ml of reagent water for analysis.

8.0 QUALITY CONTROL

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a method blank that all glassware and reagents are interference-free. Each time a set of samples is

extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis.

9.0 METHOD PERFORMANCE AND SPECIFIC QUALIFICATION

9.1 This procedure is self-qualifying due to dependence on analytical standards and to demonstrate routinely a signal to noise of greater than 20:1. It is qualified additionally through quality control samples and by Independent Technical review.

REFERENCES

1. HEADSPACE, SW-846, Method 3810, Test Methods for Evaluating Solid Waste, Third Edition, United States Environmental Protection Agency, November 1986.

2. Hachenberg, H. and A. Schmidt, Gas Chromatographic Headspace Analysis, Philadelphia: Hayden & Sons Inc., 1979.

3. Friant, S. L. and I. H. Suffet, "Interactive Effects of Temperature, Salt Concentration and pH on Headspace Analysis for Isolating Volatile Trace Organics in Aqueous Environmental Samples," Anal. Chem. 51, 2167-2172, 1979.

TABLE 1: Determination of GC/MS Purge-and-Trap Method

X Factor	Approximate Concentration Range[a]	Analyze by
0-1.0	0-1,000 ug/kg	Low-level method
>1.0	>1,000 ug/kg	High-level method

[a] This concentration range is based upon the response of aromatics to GC/FID. The concentration for halomethanes is 20x higher, and haloethanes 10x higher, when comparing GC/FID responses.

TABLE 2: Quantity of Methanol Extract Required for Analysis of High-Level Soil/Sediments

X Factor	Approximate Concentration Range[a]	Volume of Methanol Extract[b]
0.25-5.0	500-10,000 ug/kg	100 ul
0.5-10.0	1,000-20,000 ug/kg	50 ul
2.5-50.0	5,000-100,000 ug/kg	10 ul
12.5-250	25,000-500,000 ug/kg	100 ul of 1/50 dilution[c]

[a] Actual concentration ranges could be 10 to 20 times higher than this if the compounds are halogenated and the estimates are from GC/FID.

[b] The volume of methanol added to 5 mL of water being purged should be 100 uL. Therefore if the amount of methanol extract required is less

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-332, SCREENING OF HEXADECANE EXTRACTS FOR VOLATILE ORGANIC COMPOUNDS BY CLP METHOD

APPLICABILITY

This procedure applies to the gas chromatograph/flame ionization detector screening analysis of hexadecane extracts of water and solid material samples. The purpose of the screen is to determine conditions for the sample preparation for the gas chromatograph/mass spectrometry measurement of volatile organic compounds. This procedure is taken directly from the USEPA CLP Statement of Work for Organic Analysis, 2/88.

DEFINITIONS

None

RESPONSIBLE STAFF

Cognizant Staff
Analyst

PROCEDURE

See Attachment 1 for the detailed screening procedure. If sample dose rate is greater than 300 mR, method PNL-ALO-330 will be followed.

The instrumentation used in this analysis is a Hewlett-Packard 5890 gas chromatograph with a flame ionization detector. Data are recorded and processed with an electronic chromatographic peak integrator.

QUALITY CONTROL

This procedure is optional and is used as a guide only with no analytical data resulting. If this screening is used, it is important to follow these sections in Attachment 1:

Section 3, Reagents.

Section 4, Limitations.

Author	Date	Project Mgr.	Date	QAD Representative	Date
[signature]	3-21-91	B.M. Gillespie	3-21-91	[signature]	3/21/91
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
[signature]	3-21-91	[signature]	3-21-91		

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Section 5, Extract Screening.

REFERENCES

USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, 2/88, pages D-11/VOA through D-13/VOA of Exhibit D.

1. Summary of Method

1.1 The hexadecane extracts of water and soil/sediment are screened on a gas chromatograph/flame ionization detector (GC/FID). The results of the screen will determine if volatile organics are to be analyzed by low or medium level GC/MS procedures if the sample is a soil/sediment, or to determine the appropriate dilution factor if the sample is water.

2. Apparatus and Materials

2.1 Gas chromatograph - An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

2.1.1 Above-described GC, equipped with flame ionization detector.

2.1.2 GC column - 3 m x 2 mm ID glass column packed with 10% OV-101 on 100-120 mesh Chromosorb W-HP (or equivalent). The column temperature should be programmed from 80°C to 280°C at 16°C/min. and held at 280°C for 10 minutes.

3. Reagents

3.1 Hexadecane - pesticide residue analysis grade or equivalent.

4. Limitations

4.1 The flame ionization detector varies considerably in sensitivity when comparing aromatics and halogenated methanes and ethanes. Halomethanes are approximately 20 X less sensitive than aromatics and haloethanes approximately 10 X less sensitive. Low molecular weight, water soluble solvents e.g. alcohols and ketones, will not extract from the water, and therefore will not be detected by the GC/FID.

4.2 Following are two options for interpreting the GC/FID chromatogram.

4.2.1 Option A is to use standard mixture #1 containing the aromatics to calculate an approximate concentration of the aromatics in the sample. Use this information to determine the proper dilution for purge and trap if the sample is a water or whether to use the low or medium level GC/MS purge and trap methods if the sample is a soil/sediment (see Table 1, paragraph 6.2.1.3 for guidance). This should be the best approach, however, the aromatics may be absent or obscured by higher concentrations of other purgeables. In these cases, Option B may be the best approach.

4.2.2 Option B is to use standard mixture #2 containing nonane and dodecane to calculate a factor. Use the factor to calculate a dilution for purge and trap of a water sample or to determine whether to use the low or medium level GC/MS purge and trap methods for soil/sediment samples (see Table 1, paragraph

6.2.1.3 for guidance). All purgeables of interest have retention times less than the n-dodecane.

5. Extract Screening

5.1 External standard calibration - Standardize the GC/FID each 12 hr. shift for half scale response. This is done by injecting 1-5 uL of the extracts that contain approximately 10 ng/uL of the mix #1 and mix #2 compounds, prepared in paragraph 5.3.1 of Section II, Part B. Use the GC conditions specified in 2.1.2.

5.2 Inject the same volume of hexadecane extract as the extracted standard mixture in 5.1. Use the GC conditions specified in 2.1.2.

6. Analytical Decision Point

6.1 Water

6.1.1 Compare the chromatograms of the hexadecane extract of the sample with those of the reagent blank and extract of the standard.

6.1.1.1 If no peaks are noted, other than those also in the reagent blank, analyze a 5 mL water sample by purge and trap GC/MS.

6.1.1.2 If peaks are present prior to the n-dodecane and the aromatics are distinguishable, follow Option A (4.2.1).

6.1.1.3 If peaks are present prior to the n-dodecane but the aromatics are absent or indistinguishable, use Option B as follows: If all peaks are ≤3% of the n-nonane, analyze a 5 mL water sample by purge and trap GC/MS. If any peaks are ≥3% of the n-nonane, measure the peak height or area of the major peak and calculate the dilution factor as follows:

$$\frac{\text{Peak area of sample major peak}}{\text{Peak area of n-nonane}} \times 50 = \text{dilution factor}$$

The water sample will be diluted using the calculated factor just prior to purge and trap GC/MS analysis.

6.2 Soil/Sediment

6.2.1 Compare the chromatograms of the hexadecane extract of the sample with those of the reagent blank and extract of the standard.

6.2.1.1 If no peaks are noted, other than those also in the reagent blank, analyze a 5 g sample by low level GC/MS.

6.2.1.2 If peaks are present prior to the n-dodecane and the aromatics are distinguishable, follow Option A (paragraph 4.2.1) and the concentration information in Table 1, paragraph 6.2.1.3, to determine whether to analyze by low or medium level method.

6.2.1.3 If peaks are present prior to the n-dodecane but the aromatics are absent or indistinguishable, use Option B as follows: Calculate a factor using the following formula:

$$\frac{\text{peak area of sample major peak}}{\text{peak area of n-nonane}} = \text{X Factor}$$

Table 1 - Determination of GC/MS Purge & Trap Method

X Factor	Analyze by	Approximate Concentration Range* (ug/kg)
0-1.0	low level method	0-1,000
>1.0	medium level method	>1,000

* This concentration range is based on the response of aromatics to GC/FID. When comparing GC/FID responses, the concentration for halomethanes is 20X higher, and that for haloethanes 10X higher.

6.3 Sample Analysis

Proceed to Section IV, GC/MS Analysis of Volatiles.

TABLE 1. DETERMINATION OF GC/MS PURGE-AND-TRAP METHOD

X Factor	Approximate Concentration Range [a]	Analyze by
0-1.0	0-1,000 ug/kg	Low-level method
>1.0	>1,000 ug/kg	High-level method

[a] This concentration range is based upon the response of aromatics to GC/FID. The concentration for halomethanes is 20x higher, and haloethanes 10x higher, when comparing GC/FID responses.

TABLE 2. QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-LEVEL SOIL/SEDIMENTS

X Factor	Approximate Concentration Range [a]	Volume of Methanol Extract [b]
0.25-5.0	500-10,000 ug/kg	100 ul
0.5-10.0	1,000-20,000 ug/kg	50 ul
2.5-50.0	5,000-100,000 ug/kg	10 ul
12.5-250	25,000-500,000 ug/kg	100 uL of 1/50 dilution [c]

[a] Actual concentration ranges could be 10 to 20 times higher than this if the compounds are halogenated and the estimates are from GC/FID.

[b] The volume of methanol added to 5 mL of water being purged should be 100 uL. Therefore if the amount of methanol extract required is less than 100 uL, additional methanol should be added to maintain the constant 100-uL volume.

[c] Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

INTERIM CHANGE NOTICE
ICN

ICN-PNL-ALO-335.2 R0
PAGE 1 OF 1

A. Document Number: PNL-ALO-335 Revision Number: 0

Document Title: GC/MS Analysis of Volatile Organic Compounds

Document's Original Author: RW Stromatt

Effective Date of ICN: 10/26/92

Change Requested by: GA Ross

B. Action:

Add to the end of Section 7.1.9 and 7.2.2.1 this sentence:

..., optional heated (40°C) purge may be used, provided the initial and continuing calibrations are obtained under the same conditions.

Pen and ink changes.

C. Effect of Change:

Higher purge efficiency, better recovery and more reproducible results, especially with polar volatiles, such as ketones are obtained with the heated purge required for soil analysis.

D. Reason for Change/Description of Change:

To allow the heated purge to be employed with low level water and medium level soil analyses. This change gives more accurate and better reproducibility for polar compounds such as acetone, 2-Butanone.

E. Approval Signatures
(Please sign and Date)

Type of Change (Check (✓) one)

(✓)Minor Change ( )Major Change

QP Concurrence: TL Ehlert TL Ehlert Date: 10/23/92

Approval Authority: AG King AG King Date: 10/28/92

Other Approvals: RW Stromatt RW Stromatt Date: 10-26-92

: EW Hoppe Date:

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-335-1
Page 1 of 1

A. Document Number: PNL-ALO-335 Revision Number: 0
Document Title: GC/MS ANALYSIS OF VOLATILE ORGANIC COMPOUNDS
Document's Original Author: RW Stromatt

Effective Date of ICN: 4/8/91

Change Requested By: R.W Stromatt

B. Action:

Replace Applicability Section with that attached.

Pen and ink corrections on original.

C. Effect of Change:

To meet 200-BP-1 requirements

D. Reason for Change/Description of Change

Reason for change - To meet 200-BP-1 client request

Description of change - See attached

E. Approval Signatures

(Please Sign and Date)

Type of Change: (Check (✓) one)

(X) Minor Change ( ) Major Change

Process Quality ~~QSTAR~~ Department Concurrence: GK Goerbe Date: 3/21/91

Approval Authority: [signature] Date: 3/21/91

Other Approvals: B M Gillespin Date: 3/21/91

: _____ Date: / /

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-335, GC/MS ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

APPLICABILITY

This procedure applies to the determination of volatile organic compounds that can be extracted from a medium level solid (soil/sediment) sample, or purged from a water sample or a low level solid sample. The method involved sweeping the volatiles from the sample into a sorbent column where the volatiles are trapped. After purging the sample is complete, the trap column is heated and back flushed to drive the volatiles onto a GC column for the GC/MS analysis. The compounds covered by this procedure (target compounds) and their contract required quantitation limits (CRQL) are listed in Exhibit C. Concentrations and identifications are estimated for non-target compounds. The procedure is in the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) 2/88.

Problems with this procedure are caused primarily by contamination from organic compound and solvent vapors in the laboratory and losses of the volatiles due to improper sample handling.

DEFINITIONS

None

RESPONSIBLE STAFF

Cognizant Scientist
Analyst

PROCEDURE

See Attachment 1 for the detailed procedure for this GC/MS analysis for volatile organic analysis.

The instrumentation used in this analysis is the Hewlett-Packard HP5890 gas chromatograph and HP5990 mass spectrometer along with Hewlett-Packard printer and terminal peripherals. Telemar purge and trap instrumentation is used for sample separation and concentration. The HP1000 RTE series computer is used as the system controller, data processor, and data report generator.

Author	Date	Project Mgr.	Date	QAD Representative	Date
R W Hammond	7/28/89			S English	7-28-89
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
E L Hoppe	7-28-89	Walter C. Mackie	7/28/89		

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QUALITY CONTROL

See Attachment 1 for the detailed quality control procedure.

REFERENCES

USEPA Control Laboratory Program Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, 2/88, pages D-15/VOA through D-38/VOA of Exhibit D, E-11/VOA through E-27/VOA , of Exhibit E and C-2 and C-3 of Exhibit C.

Target Compound List (TCL) and Contract Required Quantitation Limits (CROL)*

Volatiles	CAS Number	Quantitation Limits** Water ug/L	Low Soil/Sediment[a] ug/Kg
1. Chloromethane	74-87-3	10	10
2. Bromomethane	74-83-9	10	10
3. Vinyl Chloride	75-01-4	10	10
4. Chloroethane	75-00-3	10	10
5. Methylene Chloride	75-09-2	5	5
6. Acetone	67-64-1	10	10
7. Carbon Disulfide	75-15-0	5	5
8. 1,1-Dichloroethene	75-35-4	5	5
9. 1,1-Dichloroethane	75-34-3	5	5
10. 1,2-Dichloroethene (total)	540-59-0	5	5
11. Chloroform	67-66-3	5	5
12. 1,2-Dichloroethane	107-06-2	5	5
13. 2-Butanone	78-93-3	10	10
14. 1,1,1-Trichloroethane	71-55-6	5	5
15. Carbon Tetrachloride	56-23-5	5	5
16. Vinyl Acetate	108-05-4	10	10
17. Bromodichloromethane	75-27-4	5	5
18. 1,2-Dichloropropane	78-87-5	5	5
19. cis-1,3-Dichloropropene	10061-01-5	5	5
20. Trichloroethene	79-01-6	5	5
21. Dibromochloromethane	124-48-1	5	5
22. 1,1,2-Trichloroethane	79-00-5	5	5
23. Benzene	71-43-2	5	5
24. trans-1,3-Dichloropropene	10061-02-6	5	5
25. Bromoform	75-25-2	5	5
26. 4-Methyl-2-pentanone	108-10-1	10	10
27. 2-Hexanone	591-78-6	10	10
28. Tetrachloroethene	127-18-4	5	5
29. Toluene	108-88-3	5	5
30. 1,1,2,2-Tetrachloroethane	79-34-5	5	5

(continued)

Volatiles	CAS Number	Quantitation Limits** Water ug/L	Low Soil/Sediment[a] ug/Kg
31. Chlorobenzene	108-90-7	5	5
32. Ethyl Benzene	100-41-4	5	5
33. Styrene	100-42-5	5	5
34. Xylenes (Total)	1330-20-7	5	5

[a] Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Volatile TCL Compounds are 125 times the individual Low Soil/Sediment CRQL.

* Specific quantitation limits are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

** Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher.

1. Summary of Methods

1.1 Water samples

An inert gas is bubbled through a 5 mL sample contained in a specifically 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 column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

An aliquot of the sample is diluted with reagent water when dilution is necessary. A 5 mL aliquot of the dilution is taken for purging.

1.2 Soil/Sediment Samples

1.2.1 Low Level. An inert gas is bubbled through a mixture of a 5 g sample and reagent water contained in a suggested specially designed purging chamber (illustrated in Figure 5) at elevated temperatures. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

1.2.2 Medium Level. A measured amount of soil is extracted with methanol. A portion of the methanol extract is diluted to 5 mL with reagent water. An inert gas is bubbled through this solution in a specifically designed purging chamber at ambient temperature. The purgeables are effectively transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

2. Interferences

2.1 Impurities in the purge gas, organic compounds out-gassing 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 contamination under the conditions of the analysis by running laboratory reagent blanks as described in Exhibit E. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

2.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling. A holding blank prepared from reagent water and carried through the holding period and the analysis protocol serves as a check on such contamination. One holding blank per case should be analyzed. Data must be retained by laboratory and made available for inspection during on-site evaluations.

2.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash out 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 subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

2.4 The laboratory where volatile analysis is performed should be completely free of solvents.

3. Apparatus and Materials

3.1 Micro syringes - 25 uL and larger, 0.006 inch ID needle.

3.2 Syringe valve - two-way, with Luer ends (three each), if applicable to the purging device.

3.3 Syringe - 5 mL, gas tight with shut-off valve.

3.4 Balance-Analytical, capable of accurately weighing ± 0.0001 g. and a top-loading balance capable of weighing ± 0.1 g.

3.5 Glassware

3.5.1
- o Bottle - 15 mL, screw cap, with Teflon cap liner.
- o Volumetric flasks - class A with ground-glass stoppers.
- o Vials - 2 mL for GC autosampler.

3.6 Purge and trap device - The purge and trap device consists of three separate pieces of equipment; the sample purger, trap and the desorber. Several complete devices are now commercially available.

3.6.1 The sample purger must be designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no

more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be utilized provided equivalent performance is demonstrated.

3.6.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. The trap must be packed to contain the following minimum lengths of absorbents: 15 cm of 2,6-diphenylene oxide polymer (Tenax-GC 60/80 mesh) and 8 cm of silica gel (Davison Chemical, 35/60 mesh, grade 15, or equivalent). The minimum specifications for the trap are illustrated in Figure 2.

3.6.3 The desorber should be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 180°C and the remaining sections should not exceed 220°C during bakeout mode. The desorber design, illustrated in Figure 2, meets these criteria.

3.6.4 The purge and trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3 and 4.

3.6.5 A heater or heated bath capable of maintaining the purge device at 40°C ± 1°C.

3.7 GC/MS system

3.7.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, and gases.

3.7.2 Column - 6 ft long x 0.1 in ID glass, packed with 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent. NOTE: Capillary columns may be used for analysis of volatiles, as long as the Contractor uses the instrumental parameters in EPA Method 524.2 as guidelines, uses the internal standards and surrogates specified in this contract, and demonstrates that the analysis meets all of the performance and QA/QC criteria contained in this contract.

3.7.3 Mass spectrometer - Capable of scanning from 35 to 260 amu every 3 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the gas chromatograph inlet.

3.7.4 GC/MS interface - Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points at 50 ng or less per injection for each of the parameters of interest and achieves all acceptable performance criteria (Exhibit E) may be used. Gas chromatograph to mass spectrometer interfaces

constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

3.7.5 Data system - A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

4. Reagents

4.1 Reagent water - Reagent water is defined as water in which an interferent is not observed at or above the CRQL of the parameters of interest.

4.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

4.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

4.1.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

4.2 Sodium thiosulfate - (ACS) Granular.

4.3 Methanol - Pesticide quality or equivalent.

4.4 Stock standard solutions - Stock standard solutions may be prepared from pure standard materials or purchased and must be traceable to EMSL/LV supplied standards. Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate.

4.4.1 Place about 9.8 mL of methanol into a 10.0 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

4.4.2 Add the assayed reference material as described below.

4.4.2.1 Liquids - Using a 100 uL syringe, immediately add two or more drops of assayed reference material to the flask then reweigh. The liquid must fall

directly into the alcohol without contacting the neck of the flask.

4.4.2.2 Gases - To prepare standards for any of the four halocarbons that boil below 30°C (bromomethane, chloroethane, chloromethane, and vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief value and direct a gentle stream of gas into the methanol meniscus.

4.4.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared standards may be used at any concentration if they are certified by the manufacturer. Commercial standards must be traceable to EMSL/LV-supplied standards.

4.4.4 Transfer the stock standard solution into multiple Teflon-sealed screw-cap bottles. Store with no headspace at -10°C to -20°C and protect from light. Once one of the bottles containing the standard solution has been opened, it may be used for at most one week.

4.4.5 Prepare fresh standards every two months for gases or for reactive compounds such as styrene. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

4.5 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. (See GC/MS Calibration in Exhibit E). Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

4.6 Surrogate standard spiking solution. Prepare stock standard solutions for toluene-d_8, p-bromofluorobenzene, and 1,2-dichloroethane-d_4 in methanol as described in paragraph 4.4. Prepare a surrogate standard spiking solution from these stock standards at a concentration of 250 ug/10 mL in methanol.

4.7 Purgeable Organic Matrix Standard Spiking Solution

4.7.1 Prepare a spiking solution in methanol that contains the following compounds at a concentration of 250 ug/10.0 mL:

Purgeable Organics
1,1-dichloroethene
trichloroethene
chlorobenzene
toluene
benzene

4.7.2 Matrix spikes also serve as duplicates; therefore, add an aliquot of this solution to each of two portions from one sample chosen for spiking.

4.8 BFB Standard - Prepare a 25 ng/uL solution of BFB in methanol.

4.9 Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10°C to -20°C in screw-cap amber bottles with teflon liners.

5. Calibration

5.1 Assemble a purge and trap device that meets the specification in paragraph 3.6. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 cm^3/min. Daily, prior to use, condition the traps for 10 minutes while backflushing at 180°C with the column at 220°C.

5.2 Connect the purge and trap device to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate parameters equivalent to those in paragraph 7.1.2. Calibrate the purge and trap-GC/MS system using the internal standard technique (paragraph 5.3).

5.3 Internal standard calibration procedure. The three internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5, at 50 ug/L at time of purge. Separate initial and continuing calibrations must be performed for water samples, and medium level soil samples.

5.3.1 Prepare calibration standards at a minimum of five concentration levels for each TCL parameter and each surrogate compound. The concentration levels are specified in Exhibit E. Standards may be stored up to 24 hours, if held in sealed vials with zero headspace at -10°C to -20°C and protected from light. If not so stored, they must be discarded after an hour.

5.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in paragraphs 4.4 and 4.5. It is recommended that the secondary dilution standard be prepared at a concentration of 25 ug/mL of each internal standard compound. The addition of 10 uL of this standard to

5.0 mL of sample or calibration standard would be equivalent of 50 ug/L.

5.3.3 Tune the GC/MS system to meet the criteria in Exhibit E by injecting BFB. Analyze each calibration standard, according to paragraph 7, adding 10 uL of internal standard spiking solution directly to the syringe. Tabulate the area response of the characteristic ions against concentration for each compound and internal standard and calculate relative response factors (RRF) for each compound using equation 1.

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

Where:

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

A_{is} - Area of the characteristic ion for the specific internal standard from Exhibit E.

C_{is} - Concentration of the internal standard.

C_x - Concentration of the compound to be measured.

5.3.4 The average relative response factor ($\overline{RRF}$) must be calculated for all compounds. A system performance check must be made before this calibration curve is used. Five compounds (the system performance check compounds) are checked for a minimum average relative response factor. These compounds (the SPCC) are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. Six compounds (the calibration check compounds, CCC) are used to evaluate the curve. These compounds the (CCC) are 1,1-Dichloroethene, Chloroform, 1,2,-Dichloropropane, Toluene, Ethylbenzene, and Vinyl Chloride. Calculate the % Relative Standard Deviation (%RSD) of RRF values over the working range of the curve. A minimum %RSD for each CCC must be met before the curve is valid.

$$\%RSD = \frac{\text{Standard deviation}}{\text{mean}} \times 100$$

See instructions for Form VI, Initial Calibration Data for more details.

5.3.5 Check of the calibration curve must be performed once every 12 hours. These criteria are described in detail in the instructions for Form VII, Continuing Calibration Check. (see Exhibit B, Section III). The minimum relative response factor for the system performance check compounds must be checked. If this criteria is met, the relative response factor of all

compounds are calculated and reported. A percent difference of the daily relative response factor (12 hour) compared to the average relative response factor from the initial curve is calculated. The maximum percent difference allowed for each compound flagged as 'CCC' in Form VII is checked. Only after both these criteria are met can sample analysis begin.

5.3.6 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each standard. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is necessary.

6. GC/MS Operating Conditions

6.1 These performance tests require the following instrumental parameters:

Electron Energy:	70 Volts (nominal)
Mass Range:	35 - 260
Scan Time:	to give at least 5 scans per peak and not to exceed 3 seconds per scan.

7. Sample Analysis

7.1 Water Samples

7.1.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.1.2 Recommended operating conditions for the gas chromatograph Packed column conditions: Carbopak B (60/80 mesh) with 1% SP-1000 packed in a 6 foot by 2 mm ID glass column with helium carrier gas at a flow rate of 30 cm^3/min. Column temperature is isothermal at 45°C for 3 minutes, then programmed at 8°C per minute to 220°C and held for 15 minutes. Injector temperature is 200-225°C. Source temperature is set according to the manufacturer's specifications. Transfer line temperature is 250-300°C. The recommended carrier gas is helium at 30 cm^3/sec. (See EPA Method 5.2.4.2 for capillary column condition.)

7.1.3 After achieving the key ion abundance criteria, calibrate the system daily as described in Exhibit E.

7.1.4 Adjust the purge gas (helium) flow rate to 25-40 cm^3/min. Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.

7.1.5 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the sample for future analysis so if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such a time when the analyst has determined that the first sample has been analyzed properly. Filling one 20 mL syringe would allow the use of only one syringe. If a second analysis is needed from the 20 mL syringe, it must be analyzed within 24 hours. Care must also be taken to prevent air from leaking into the syringe.

7.1.6 The purgeable organics screening procedure (Section III), if used, will have shown the approximate concentrations of major sample components. If a dilution of the sample was indicated, this dilution shall be made just prior to GC/MS analysis of the sample. All steps in the dilution procedure must be performed without delays until the point at which the diluted sample is in a gas tight syringe.

7.1.6.1 The following procedure will allow for dilutions near the calculated dilution factor from the screening procedure:

7.1.6.1.1 All dilutions are made in volumetric flasks (10 mL to 100 mL).

7.1.6.1.2 Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.1.6.1.3 Calculate the approximate volume of reagent water which will be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

7.1.6.1.4 Inject the proper aliquot from the syringe prepared in paragraph 7.1.5 into the volumetric flask. Aliquots of less than 1 mL increments are prohibited. Dilute the flask to the

mark with reagent water. Cap the flask, invert, and shake three times.

7.1.6.1.5 Fill a 5 mL syringe with the diluted sample as in paragraph 7.1.5.

7.1.6.1.6 If this is an intermediate dilution, use it and repeat above procedure to achieve larger dilutions.

7.1.7 Add 10.0 uL of the surrogate spiking solution (4.6) and 10.0 uL of the internal standard spiking solution (5.3.2) through the valve bore of the syringe, then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 uL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

7.1.8 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.1.9 Close both valves and purge the sample for 11.0 ± 0.1 minutes at ambient temperature.

7.1.10 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas between 20 and 60 cm^3/min for four minutes. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial temperature of 45°C.

7.1.11 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water to avoid carryover of pollutant compounds.

7.1.12 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device 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. Trap temperatures up to 220°C may be employed, however the higher temperature will shorten the useful life of the trap. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.1.13 If the initial analysis of a sample or a dilution of a sample has concentration of TCL compounds that exceeds the initial

calibration range, the sample must be reanalyzed at a higher dilution. Note: For total xylenes, where three isomers are quantified as two peaks, the calibration range of each peak should be considered separately, e.g., a diluted analysis is not required for total xylenes unless the concentration of either peak separately exceeds 200 ug/L. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is used, document the reasons in the Case Narrative. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.1.14 For water samples, add 10 uL of the matrix spike solution (paragraph 4.7) to the 5 mL of sample purged. Disregarding any dilutions, this is equivalent to a concentration of 50 ug/L of each matrix spike standard.

7.1.15 All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.2 Soil/Sediment Samples

Two approaches may be taken to determine whether the low level or medium level method may be followed.

- Assume the sample is low level and analyze a 5 g sample.
- Use the X factor calculated from the optional hexadecane screen (Section III, paragraph 6.2.1.3).

If peaks are saturated from the analysis of a 5 g sample, a smaller sample size must be analyzed to prevent saturation. However, the smallest sample size permitted is 1 g. If smaller than 1 g sample size is needed to prevent saturation, the medium level method must be used.

7.2.1 Low Level Soil Method

The low level soil method is based on purging a heated sediment/ soil sample mixed with reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples.

Use 5 grams of sample or use the X Factor to determine the sample size for purging.

- If the X Factor is 0 (no peaks noted on the hexadecane screen), analyze a 5 g sample.
- If the X Factor is between 0 and 1.0, analyze a minimum of a 1 g sample.

7.2.1.1 The GC/MS system should be set up as in 7.1.2-7.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and sample. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-level method. Follow the initial and daily calibration instructions (5.3) except for the addition of a 40°C purge temperature.

7.2.1.2 To prepare the reagent water containing the surrogates and internal standards, remove the plunger from a 5 mL "Luerlock" type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 uL each of the surrogate spiking solution (4.6) and the internal standard solution to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together). The addition of 10 uL of the surrogate spiking solution to 5 g of soil/sediment is equivalent to 50 ug/kg of each surrogate standard.

7.2.1.3 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in 7.2.1 into a tared purge device. Use a top loading balance. Note and record the actual weight to the nearest 0.1 g.

7.2.1.4 Immediately after weighing the sample, weigh 5-10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\frac{\text{Percent moisture}}{\text{g of sample-g of dry sample}} \quad \text{X } 100 = \text{\% moisture}$$

7.2.1.5 Add the spiked reagent water to the purge device and connect the device to the purge and trap system. Note: Prior to the attachment of the purge device, steps 7.2.1.2 and 7.2.1.3 must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.2.1.6 Heat the sample to 40°C ± 1°C and purge the sample for 11.0 ± 0.1 minutes.

7.2.1.7 Proceed with the analysis as outlined in 7.1.10 7.1.13. Use 5 mL of the same reagent water as the reagent blank.

7.2.1.8 For low level soils/sediment add 10 uL of the matrix spike solution (4.7) to the 5 mL of water (7.2.1.2). The concentration for a 5 g sample would be equivalent to 50 ug/kg of each matrix spike standard.

7.2.2 Medium Level Soil Method

The medium level soil method is based on extracting the soil/sediment sample with methanol. An aliquot of the methanol extract is added to reagent water containing the surrogate and internal standards. This is purged at ambient temperature. All samples with an X Factor >1.0 should be analyzed by the medium level method. If saturated peaks occurred or would occur when a 1 g sample was analyzed, the medium level method must be used.

7.2.2.1 The GC/MS system should be set up as in 7.1.2 - 7.1.4. This should be done prior to the addition of the methanol extract to reagent water. Initial and continuing calibrations (5.3) are performed by adding standards in methanol to reagent water and purging at ambient temperature.

7.2.2.2 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh 4 g (wet weight) into a tared 15 mL vial. Use a top loading balance. Note and record the actual weight to the nearest 0.1 g. Determine the percent moisture as in 7.2.1.4.

7.2.2.3 Quickly add 9.0 mL of methanol, then 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes. NOTE: Steps 7.2.2.1 and 7.2.2.2 must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.2.2.4 Using a disposable pipette, transfer approximately 1 mL of extract into a GC vial for storage. The remainder may be disposed of. Transfer approximately 1 mL of the reagent methanol to a GC vial for use as the method blank for each case or set of 20 samples, whichever is more frequent. These extracts may be stored in the dark at 4°C (±2°C) prior to analysis.

The addition of a 100 uL aliquot of each of these extracts in paragraph 7.2.2.6 will give a concentration equivalent to 6,200 ug/kg of each surrogate standard.

7.2.2.5 The following table can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. If the Hexadecane screen procedure was followed, use the X factor (Option B) or the estimated concentration (Option A) to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low level analysis to determine the appropriate volume. If the sample was submitted as a medium level sample, start with 100 uL.

All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of linear range of the curve.

X Factor	Estimated Concentration Range[1] ug/kg	Take this Volume of Methanol Extract[2] uL
0.25 - 5.0	500 - 10,000	100
0.5 - 10.0	1000 - 20,000	50
2.5 - 50.0	5000 - 100,000	10
12.5 - 250	25,000 - 500,000	100 of 1/50 dilution[3]

Calculate appropriate dilution factor for concentrations exceeding the table.

1 Actual concentration ranges could be 10 to 20 times higher than this if the compounds are halogenated and the estimates are from GC/FID.

2 The volume of methanol added to the 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 uL added to the syringe.

3 Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

7.2.2.6 Remove the plunger from a 5 mL "Luerlock" type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5 mL to allow volume for the addition of sample and standards. Add 10 uL of the internal standard solution. Also add the volume of methanol extract determined in 7.2.2.5 and a volume of methanol solvent to total 100 uL (excluding methanol in standards).

7.2.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.2.2.8 Proceed with the analysis as outlined in 7.1.9 - 7.1.13. Analyze all reagent blanks on the same instrument as the samples. The standards should also contain 100 uL of methanol to simulate the sample conditions.

7.2.2.9 For a matrix spike in the medium level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (4.6), and 1.0 mL of matrix spike solution (4.7) in paragraph 7.2.2.2. This results in a 6,200 ug/kg concentration of each matrix spike standard when added to a 4 g sample. Add a 100 uL aliquot of this extract to 5 mL of water for purging (as per paragraph 7.2.2.6).

8. Qualitative Analysis

8.1 The compounds listed in the Target Compound List (TCL), Exhibit C, shall be identified by an analyst competent in the interpretation of mass spectra (see Bidder Responsibility description) by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

8.1.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

8.1.2 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the Contractor's GC/MS meets the daily tuning requirements for BFB. These standard spectra may be obtained from the run used to obtain reference RRTs.

8.1.3 The requirements for qualitative verification by comparison of mass spectra are as follows:

8.1.3.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant

ion in the spectrum equals 100%) must be present in the sample spectrum.

8.1.3.2 The relative intensities of ions specified in 8.1.3.1 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent).

8.1.3.3 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. In Task III, the verification process should favor false negatives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the CRQL report the actual value followed by a "J", e.g., "3J."

8.1.4 If a compound cannot be verified by all of the criteria in 8.1.3.3, but in the technical judgement of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantification in 9.

8.2 A library search shall be executed for non-TCL sample components for the purpose of tentative identification. For this purpose, the I985 release of the National Bureau of Standards Mass Spectral Library (or more recent release), containing 42,261 spectra, shall be used. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

8.2.1 Up to 10 nonsurrogate organic compounds of greatest apparent concentration not listed in Exhibit C for the purgeable organic fraction shall be tentatively identified via a forward search of the NBS mass spectral library. (Substances with responses less than 10% of the internal standard are not required to be searched in this fashion). Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

8.2.2 Guidelines for making tentative identification:

8.2.2.1 Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

8.2.2.2 The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an

abundance of 50 percent of the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)

8.2.2.3 Molecular ions present in reference spectrum should be present in sample spectrum.

8.2.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

8.2.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

8.2.3 If in the technical judgement of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e. unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

9. Quantitative Analysis

9.1 TCL components identified shall be quantified by the internal standard method. The internal standard used shall be that which is listed in Exhibit E, Table 2.1. The EICP area of the characteristic ions of analytes listed in Tables 2 and 3 in this Section are used.

9.2 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

9.2.1 If after re-analysis, the EICP areas for all internal standards are inside the contract 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 EICPs within the contract limits.

This is considered the initial analysis and must be reported as such on all data deliverables.

9.2.2 If the re-analysis of the sample does not solve the problem, i.e., the EICP areas are outside the contract limits for both analyses, then submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the re-analysis on all data deliverables, using the sample suffixes specified in Exhibit B. Document in the Case Narrative all inspection and corrective actions taken.

9.3 The relative response factor (RRF) from the daily standard analysis is used to calculate the concentration in the sample. Use the relative response factor as determined in paragraph 5.3.3 and the equations below. When TCL compounds are below contract required quantitation limits (CRQL) but the spectra meet the identification criteria, report the concentration with a "J." For example, if CRQL is 10 ug/L and concentration of 3 ug/L is calculated, report as "3J."

Water

$$\text{Concentration ug/L} = \frac{(A_x)(I_s)}{(A_{is})(RRF)(V_o)}$$

Where:

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

A_{is} = Area of the characteristic ion for the specific internal standard from Exhibit E.

I_s = Amount of internal standard added in nanograms (ng)

V_o = Volume of water purged in milliliters (mL) (take into account any dilutions)

Sediment/Soil (medium level)

$$\text{Concentration ug/kg} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RRF)(V_i)(W_s)(D)}$$

Sediment/Soil (low level)

$$\text{Concentration (Dry weight basis) ug/kg} = \frac{(A_x)(I_s)}{(A_{is})(RRF)(W_s)(D)}$$

Where:

A_x, I_s, A_{is} = same as for water, above

V_t = Volume of total extract (uL) (use 10,000 uL or a factor of this when dilutions are made)

V_i = Volume of extract added (uL) for purging

D = $\frac{100 - \% \text{ moisture}}{100}$

W_s = Weight of sample extracted (g) or purged

9.4 An estimated concentration for non-TCL components tentatively identified shall be quantified by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used.

9.4.1 The formula for calculating concentrations is the same as in paragraph 9.3. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

9.5 Xylenes (o-,m-, & p- isomers) are to be reported as Xylenes (total). Since o- and p-Xylene overlap, the Xylenes must be quantitated as m-Xylene. The concentration of all Xylene isomers must be added together to give the total.

9.6 1,2-Dichloroethene (trans and cis stereoisomers) are to be reported as 1,2-Dichloroethene (total). The concentrations of both isomers must be added together to give the total.

9.7 Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if recovery is within limits and report on appropriate form.

9.7.1 Calculation for surrogate recovery.

$$\text{Percent Surrogate Recovery} = \frac{Q_d}{Q_a} \times 100\%$$

Where:

Q_d = quantity determined by analysis

Q_a = quantity added to sample

9.7.2 If recovery is not within limits, the following is required:

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Reanalyze the sample if none of the above reveal a problem.

9.7.3 If the reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, only

submit data from the analysis with surrogate spike recoveries within the contract limits. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

9.7.4 If the reanalysis of the sample does not solve the problem, i.e., surrogate recoveries are outside the contract limits for both analyses, then submit the surrogate spike recovery data and the sample data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables, using the sample suffixes specified in Exhibit B.

9.7.5 If the sample with surrogate recoveries outside the limits is the sample used for the matrix spike and matrix spike duplicate, and the surrogate recoveries of the matrix spike and matrix spike duplicate show the same pattern (i.e., outside the limits), then the sample, matrix spike, and matrix spike duplicate do not require reanalysis. Document in the narrative the similarity in surrogate recoveries.

Table 2

Characteristic Ions for Surrogate and Internal Standards for Volatile Organic Compounds

Compound	Primary Ion	Secondary Ion(s)
SURROGATE STANDARDS		
4-Bromofluorobenzene	95	174, 176
1,2-Dichloroethane d-4	65	102
Toluene d-8	98	70, 100
INTERNAL STANDARDS		
Bromochloromethane	128	49, 130, 51
1,4-Difluorobenzene	114	63, 88
Chlorobenzene d-5	117	82, 119

Table 3
Characteristic Ions for Volatile TCL Compounds

Parameter	Primary Ion*	Secondary Ion(s)
Chloromethane	50	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 51, 86
Acetone	43	58
Carbon disulfide	76	78
1,1-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 83, 85, 98, 100
1,2-Dichloroethene	96	61, 98
Chloroform	83	85
1,2-Dichloroethane	62	64, 100, 98
2-Butanone	72	57
1,1,1-Trichloroethane	97	99, 117, 119
Carbon tetrachloride	117	119, 121
Vinyl acetate	43	86
Bromodichloromethane	83	85
1,1,2,2-Tetrachloroethane	83	85, 131, 133, 166
1,2-Dichloropropane	63	65, 114
trans-1,3-Dichloropropene	75	77
Trichloroethene	130	95, 97, 132
Dibromochloromethane	129	208, 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Benzene	78	-
cis-1,3-Dichloropropene	75	77
Bromoform	173	171, 175, 250, 252, 254, 256
2-Hexanone	43	58, 57, 100
4-Methyl-2-pentanone	43	58, 100
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
Chlorobenzene	112	114
Ethyl benzene	106	91
Styrene	104	78, 103
Total xylenes	106	91

* The primary ion should be used unless interferences are present, in which case, a secondary ion may be used.

IV.

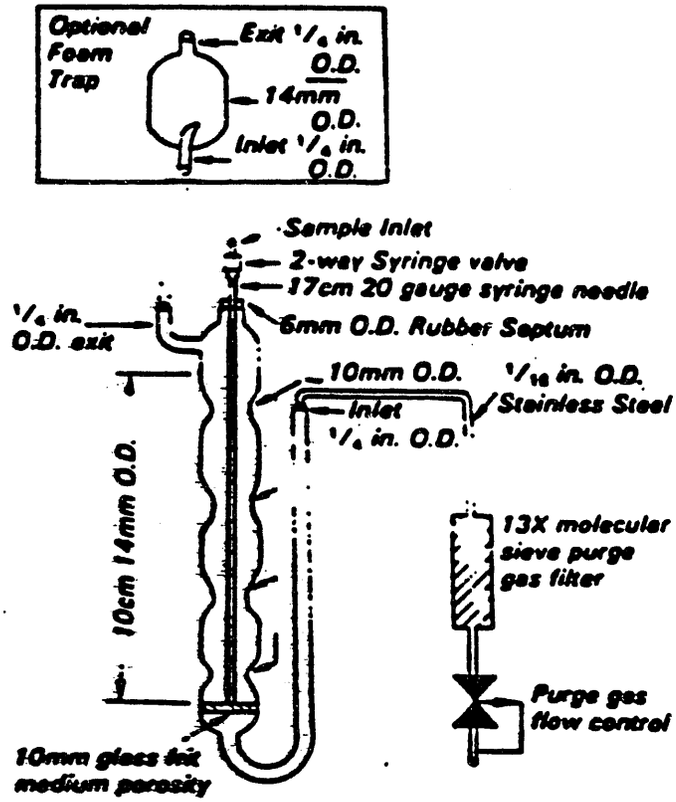

Figure 1. Purging device

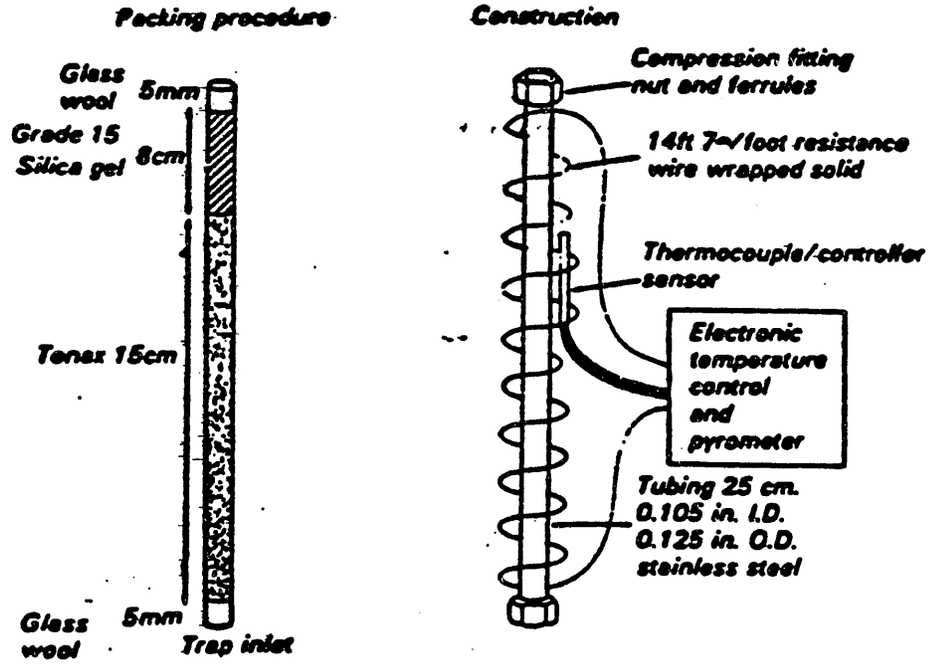

Figure 2. Trap packings and construction to include desorb capability

IV.

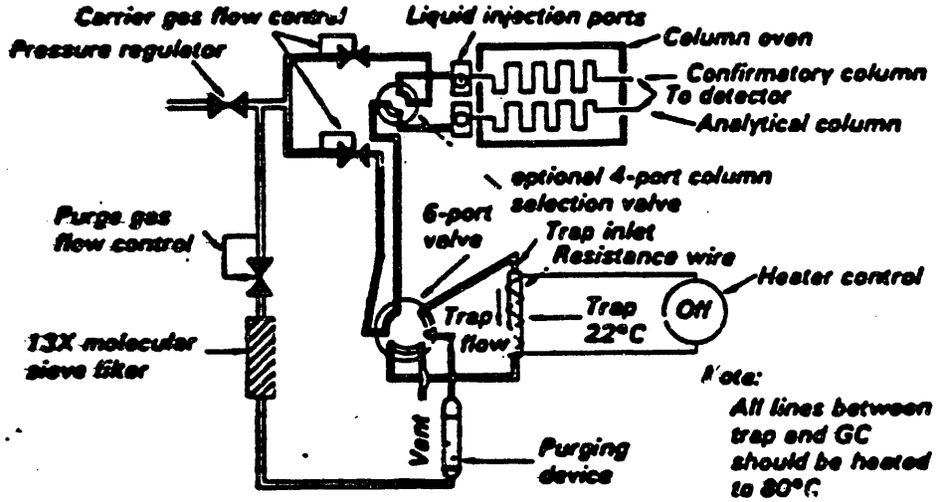

Figure 3. Schematic of purge and trap device — purge mode

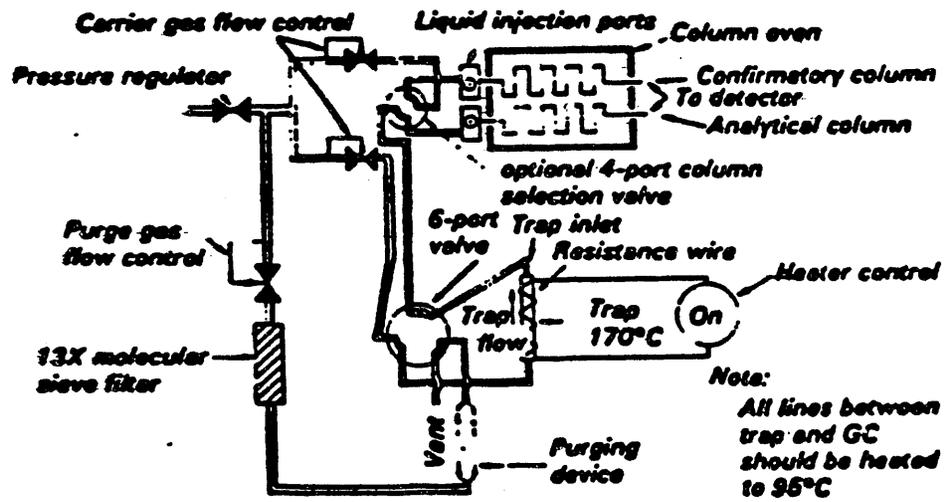

Figure 4. Schematic of purge and trap device — desorb mode

IV.

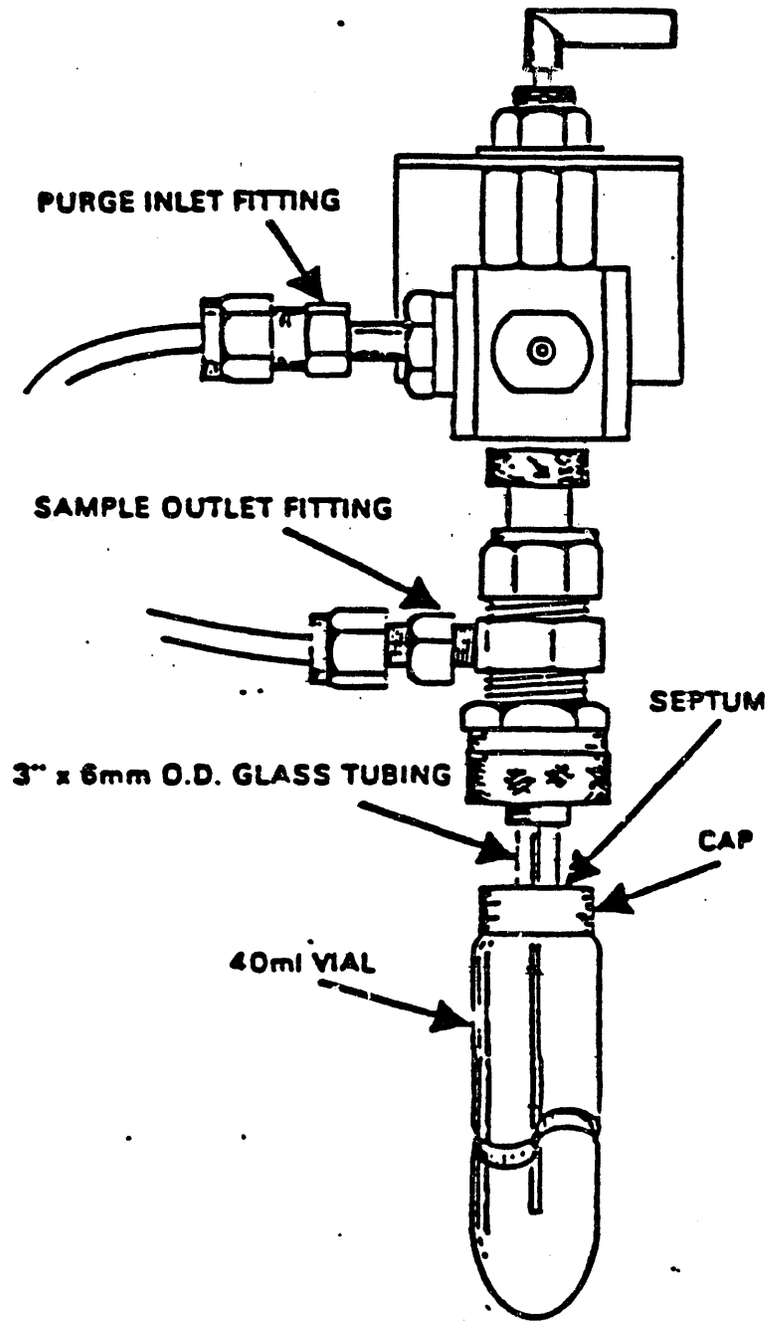

Figure 5. Low Soils Impinger

This section outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with the determination of volatile organic TCL compounds in water and soil/sediment samples. These QC operations are as follows:

- o Documentation of GC/MS Mass Calibration and Abundance Pattern
- o Documentation of GC/MS Response Factor Stability
- o Internal Standard Response and Retention Time Monitoring
- o Method Blank Analysis
- o Surrogate Spike Response Monitoring
- o Matrix Spike and Matrix Spike Duplicate Analysis

PART 1 - TUNING AND GC/MS MASS CALIBRATION

1. Summary

It is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria prior to initiating any on-going data collection. This is accomplished through the analysis of p-Bromofluorobenzene (BFB).

Definition: The twelve (12) hour time period for GC/MS system tuning, standards calibration (initial or continuing calibration criteria) and method blank analysis begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant tune. The time period ends after twelve (12) hours has elapsed according to the system clock.

1.1 p-Bromofluorobenzene (BFB)

1.1.1 Each GC/MS system used for the analysis of volatile TCL compounds must be hardware tuned to meet the abundance criteria listed in Table 1.1 for a maximum of a 50 nanogram injection of BFB. Alternately, add 50 ng of BFB solution to 5.0 ml of reagent water and analyze according to Exhibit D VOA, Section IV. BFB shall not be analyzed simultaneously with any calibration standards or blanks. This criterion must be demonstrated daily or for each twelve-hour time period, whichever is more frequent. If required, background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the contract specifications are unacceptable.

NOTE: All instrument conditions must be identical to those used in sample analysis, except that a different temperature program may be used.

1.1.2 BFB criteria MUST be met before any standards, samples, or blanks are analyzed. Any samples analyzed when tuning criteria

have not been met may require reanalysis at no cost to the Agency.

1.1.3 Whenever the Contractor takes corrective action which may change or affect the tuning criteria for BFB (e.g., ion source cleaning or repair, etc.), the tune must be verified irrespective of the twelve-hour tuning requirements.

TABLE 1.1. 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 the 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

1.2 Documentation

The Contractor shall provide documentation of the calibration in the form of a bar graph spectrum and as a mass listing.

1.2.1 The Contractor shall complete a Form V (GC/MS Tuning and Mass Calibration) each time an analytical system is tuned. In addition, all standards, samples, blanks, matrix spikes, and matrix spike duplicates analyzed during a particular tune must be summarized in chronological order on the bottom of the appropriate Form V. Detailed instructions for the completion of Form V are in Exhibit B, Section III.

PART 2 - CALIBRATION OF THE GC/MS SYSTEM

2. Summary

Prior to the analysis of samples and required 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.

2.1 Prepare calibration standards as described in Exhibit D VOA, Section IV, to yield the following specific concentrations:

2.1.1 Volatile TCL Compounds

Initial calibration of volatile TCL compounds is required at 20, 50, 100, 150 and 200 ug/L. Surrogate and internal standards shall be used with each of the calibration standards. Utilizing the analytical protocol specified in Exhibit D this will result in 100-1000 total ng analyzed. If an analyte saturates at the 200 ug/L concentration level, and the GC/MS system is calibrated to achieve a detection sensitivity of no less than 5 ug/L, the laboratory must document it in the Case Narrative, and attach a quantitation report and RIC. In this instance, the laboratory should calculate the results based on a four-point initial calibration for the specific analyte that saturates. The use of separate calibration methods which reflect the two different low and medium soil/sediment methods is required. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is used, document the reasons in the Case Narrative. Analyze all method blanks and standards under the same conditions as the samples.

2.2 The USEPA plans to develop performance based criteria for response factor data acquired during this program. To accomplish this goal, the Agency has specified both the concentration levels for initial calibration and has also specified the specific internal standard to be used on a compound-by-compound basis for quantitation (see Table 2.1). Establishment of standard calibration procedures is necessary and deviations by the Contractor will not be allowed.

2.3 Analyze each calibration standard and tabulate the area of the primary characteristic ion (Exhibit D VOA, Table 3) against concentration for each compound including all contract required surrogate compounds. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late eluting compounds usually will have much better agreement.

Using Table 2.1 and Equation 2.1, calculate the relative response factors (RRF) for each compound at each concentration level.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x} \qquad \text{Eq. 2.1}$$

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 2.1 or 2.2.

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

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

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.

2.4 A system performance check must be performed to ensure that minimum average relative response factors are met before the calibration curve is used.

2.4.1 For volatiles, the five System Performance Check Compounds (SPCCs) are: chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane and chlorobenzene. The minimum acceptable average relative response factor (RRF) for these compounds is 0.300, 0.250 for Bromoform. These compounds typically have RRFs of 0.4-0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. For instance:

- o Chloromethane - this compound is the most likely compound to be lost if the purge flow is too fast.
- o Bromoform - this compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.
- o Tetrachloroethane, 1,1-Dichloroethane - These compounds can be deteriorated by contaminated transfer lines in purge and trap systems and/or active sites in trapping materials.

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

2.5 Documentation

Once the initial calibration is validated, calculate and report the average relative response factor (RRF) and percent relative standard deviation (%RSD) for all TCL compounds. The Contractor shall complete and submit Form V (the GC/MS tune for the initial calibration) and Form VI (Initial Calibration Data) for each instrument used to analyze samples under this protocol. Detailed instructions for completion of Form VI are in Exhibit B, Section III.

2.6 Continuing Calibration

A calibration standard(s) containing all volatile TCL compounds, including all required surrogates, must be performed each twelve hours during analysis (see definition of twelve hour time period, paragraph 1. of this Section). Compare the relative response factor data from the standards each twelve hours with the average relative response

TABLE 2.2 VOLATILE CALIBRATION CHECKCOMPOUNDS

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

2.6.3 Concentration Levels for Continuing Calibration Check

The USEPA plans to evaluate the long term stability of relative response factors during this program. Standardization among contract laboratories is necessary to reach these long term goals. Along with contract specified concentrations for initial calibration, the USEPA is requiring specific concentrations for each continuing calibration standard(s).

2.6.3.1 The concentration for each volatile TCL compound in the continuing calibration standard(s) is 50 ug/L.

2.7 Documentation

The Contractor shall complete and submit a Form VII for each GC/MS system utilized for each twelve hour time period. Calculate and report the relative response factor and percent difference (%D) for all compounds. Ensure that the minimum RRF for volatile SPCCs is 0.300 and 0.250 for Bromoform. The percent difference (%D) for each CCC compound must be less than or equal to 25.0 percent. Additional instructions for completing Form VII are in Exhibit B, Section III.

PART 3 - METHOD BLANK ANALYSIS

3. Summary

A method blank is a volume of deionized, distilled laboratory water for water samples, or a purified solid matrix for soil/sediment samples, carried through the entire analytical scheme. The method blank volume or weight must be approximately equal to the sample volumes or sample weights being processed.

3.1 Method blank analysis must be performed at the following frequency:

3.1.1 For the analysis of volatile TCL compounds, a method blank analysis must be performed once for each 12-hour time period. See Part 1, paragraph 1 for the definition of the 12-hour time period.

3.2 It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

TABLE 4.1 SURROGATE SPIKING COMPOUNDS

Compounds	Fraction	Amount in Sample/Extract* (before any optional dilutions) Water	Low/Medium Soil
Toluene-d_8	VOA	50 ug	50 ug
4-Bromofluorobenzene	VOA	50 ug	50 ug
1,2-Dichloroethane-d_4	VOA	50 ug	50 ug

* At the time of injection.

4.2 Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the contract required recovery limits listed in Table 4.2.

TABLE 4.2 CONTRACT REQUIRED SURROGATE SPIKE RECOVERY LIMITS

Fraction	Surrogate Compound	Water	Low/Medium Soil
VOA	Toluene-d_8	88-110	81-117
VOA	4-Bromofluorobenzene	86-115	74-121
VOA	1,2-Dichloroethane-d_4	76-114	70-121

4.3 Treatment of surrogate spike recovery information is according to paragraphs 4.3.1 through 4.3.2.

4.3.1 Method Blank Surrogate Spike Recovery

The laboratory must take the actions listed below if recovery of any one surrogate compound in the volatiles fraction of the method blank is outside of the required surrogate spike recovery limits.

4.3.1.1 Check calculations to ensure that there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc; also check instrument performance.

4.3.1.2 Reanalyze the blank or extract if steps in 4.3.1.1 fail to reveal the cause of the noncompliant surrogate recoveries.

4.3.1.3 If the blank is a methanol extract for medium level soil samples, reextract and reanalyze the blank if steps in 4.3.1.2 fail to reveal the cause of the noncompliant surrogate recoveries.

and analysis with surrogate spike recoveries within the contract windows. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

4.3.2.1.4 If the reextraction and/or reanalysis of the sample does not solve the problem; i.e., surrogate recoveries are outside the contract windows for both analyses, then submit the surrogate spike recovery data and the sample data from both analyses according to paragraph 4.4. Distinguish between the initial analysis and the reanalysis on all data deliverables, using the sample suffixes specified in Exhibit B.

4.4 Documentation

The Contractor is required to report surrogate recovery data for the following:

- Method Blank Analysis
- Sample Analysis
- Matrix Spike/Matrix Spike Duplicate Analyses
- All sample reanalyses that substantiate a matrix effect

The surrogate spike recovery data are summarized on the Surrogate Spike Percent Recovery Summary (Form II). Detailed instructions for the completion of Form II are in Exhibit B, Section III.

PART 5 - MATRIX SPIKE/MATRIX SPIKE DUPLICATE ANALYSIS (MS/MSD)

5. Summary

In order to evaluate the matrix effect of the sample upon the analytical methodology, the USEPA has developed the standard mixes listed in Table 5.1 to be used for matrix spike and matrix spike duplicate analyses. These compounds are subject to change depending upon availability and suitability for use as matrix spikes.

5.1 MS/MSD Frequency of Analysis

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

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100 \qquad \text{Eq. 5.2}$$

where,

RPD - Relative Percent Difference

D_1 - First Sample Value

D_2 - Second Sample Value (duplicate)

5.5 Documentation

The matrix spike (MS) results (concentrations) for nonspiked volatile TCL compounds shall be reported on Form I (Organic Analysis Data Sheet) and the matrix spike percent recoveries shall be summarized on Form III (MS/MSD Recovery). These values will be used by EPA to periodically update existing performance based QC recovery limits (Table 5.2).

The results for nonspiked volatile TCL compounds in the matrix spike duplicate (MSD) analysis shall be reported on Form I (Organic Analysis Data Sheet) and the percent recovery and the relative percent difference shall be summarized on Form III (MS/MSD Recovery). The RPD data will be used by EPA to evaluate the long term precision of the analytical method. Detailed instructions for the completion of Form III are in Exhibit B, Section III.

TABLE 5.2. MATRIX SPIKE RECOVERY LIMITS

Fraction	Matrix Spike Compound	Water	Soil/Sediment
VOA	1,1-Dichloroethene	61-145	59-172
VOA	Trichlorethene	71-120	62-137
VOA	Chlorobenzene	75-130	60-133
VOA	Toluene	76-125	59-139
VOA	Benzene	76-127	66-142

PART 6 - SAMPLE ANALYSIS

6. Summary

The intent of Part 6 is to provide the Contractor with a brief summary of ongoing QC activities involved with sample analysis. Specific references are provided to help the Contractor meet specific reporting and deliverables requirements of this contract.

6.1 Sample Analysis

Samples can be analyzed upon successful completion of the initial QC activities. When twelve (12) hours have elapsed since the initial tune

6.1.2 Each analytical run must also be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound. The initial method calibration (Part 2) requires that the system should not be saturated for high response compounds at 200 ug/L for VOA TCL compounds.

6.1.2.1 If the on-column concentration of any compound in any sample exceeds the initial calibration range, that sample must be diluted, the internal standard concentration readjusted, and the sample reinjected, as described in specific methodologies in Exhibit D VOA. Note: For total xylenes, where three isomers are quantified as two peaks, the calibration of each peak should be considered separately, i.e., a diluted analysis is not required for total xylenes unless the concentration of either peak separately exceeds 200 ug/L. Secondary ion quantitation is only allowed when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the Case Narrative.

6.1.2.2 If the dilution of the sample causes any compound detected in the first analysis to be undetectable in the second analysis, then the results of both analyses shall be reported on separate Forms I, according to the instructions in Exhibit B.

6.1.3 Qualitative Analysis

The compounds listed in the Target Compound List (TCL), Exhibit C, shall be identified by an analyst competent in the interpretation of mass spectra, by comparison of the suspect mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra (Exhibit D, Section IV).

6.1.3.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample.

6.1.3.2 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/MS are required. The BFB tuning requirements listed in Part 1 of this Section must be met on that same GC/MS.

6.1.3.2.1 The requirements for qualitative verification by comparison of mass spectra are as follows:

- o All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
- o The relative intensities of ions specified in the above paragraph must agree within ±20% between the standard and sample spectra.
- o Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. When GC/MS computer data processing programs are used to obtain the sample component spectrum, both the processed and the raw spectra must be evaluated. In Task III, the verification process should favor false positives (Exhibit D, Section IV).

6.1.3.2.2 If a compound cannot be verified by all of the criteria in 6.1.3.2.1, but in the technical judgement of the mass spectral interpretation specialist the identification is correct, the Contractor shall report the identification and proceed with the quantitation.

6.1.3.3 A library search shall be executed for nonsurrogate and non-TCL sample components for the purpose of tentative identification. For this purpose, the 1985 or most recent available version of the National Bureau of Standards Mass Spectral Library, containing 42,261 spectra should be used.

6.1.4 Quantitation

6.1.4.1 TCL components identified shall be quantitated by the internal standard method. The internal standards used shall be the ones assigned in Table 2.1 of this Section. The EICP area of characteristic ions of TCL analytes are used (Exhibit D VOA, Section IV).

6.1.2 Each analytical run must also be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound. The initial method calibration (Part 2) requires that the system should not be saturated for high response compounds at 200 ug/L for VOA TCL compounds.

6.1.2.1 If the on-column concentration of any compound in any sample exceeds the initial calibration range, that sample must be diluted, the internal standard concentration readjusted, and the sample reinjected, as described in specific methodologies in Exhibit D VOA. Note: For total xylenes, where three isomers are quantified as two peaks, the calibration of each peak should be considered separately, i.e., a diluted analysis is not required for total xylenes unless the concentration of either peak separately exceeds 200 ug/L. Secondary ion quantitation is only allowed when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the Case Narrative.

6.1.2.2 If the dilution of the sample causes any compound detected in the first analysis to be undetectable in the second analysis, then the results of both analyses shall be reported on separate Forms I, according to the instructions in Exhibit B.

6.1.3 Qualitative Analysis

The compounds listed in the Target Compound List (TCL), Exhibit C, shall be identified by an analyst competent in the interpretation of mass spectra, by comparison of the suspect mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra (Exhibit D, Section IV).

6.1.3.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample.

6.1.3.2 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/MS are required. The BFB tuning requirements listed in Part 1 of this Section must be met on that same GC/MS.

6.1.4.2 An estimated concentration for non-TCL components tentatively identified shall be quantitated by the internal standard method. For quantification, the nearest internal standard free of interferences must be used.

6.1.4.3 Calculate surrogate standard recovery (see Part 4) for all surrogate compounds in all samples, blanks, matrix spikes, and matrix spike duplicates. If recovery is within contractual limits, report on Form II (see Exhibit B). If recovery is outside contractual limits, take specific steps listed in Surrogate Spike Recoveries (Part 4).

6.1.4.4 Calculate matrix spike and matrix spike duplicate percent recovery (see Part 5 of this Section) for all compounds and report results on Form III (see Exhibit B). Calculate Relative Percent Differences (RPDs) for all matrix spiking compounds and report results on Form III. Ensure that the proper frequency of MS/MSD analysis is maintained.

6.1.5 Reporting and Deliverables

Refer to Exhibit B of this Statement of Work for specific details on contract deliverables and reporting formats. Exhibit B contains specific instructions for completing all required Forms, as well as a detailed itemization of reporting and deliverables requirements. Exhibit H contains the format requirements for delivery of data in computer-readable format.

APPLICABILITY

This procedure applies to the determination of volatile organic compounds that can be extracted from a medium level solid (soil/sediment) sample, or purged from a water sample or a low level solid sample. An optional screening analysis, method PNL-ALO-330, PNL-ALO-331 or PNL-ALO-332, is used to make an estimate of organic concentration for the sample preparation steps. The method involved sweeping the volatiles from the sample into a sorbent column where the volatiles are trapped. After purging the sample is complete, the trap column is heated and back flushed to drive the volatiles onto a GC column for the GC/MS analysis. The compounds covered by this procedure (target compounds) and their contract required quantitation limits (CRQL) are listed in Exhibit C. Concentrations and identifications are estimated for non-target compounds. The procedure is in the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) 2/88.

Problems with this procedure are caused primarily by contamination from organic compound and solvent vapors in the laboratory and losses of the volatiles due to improper sample handling.

PNL-ALO-336, GC/MS ANALYSIS OF METHANOL EXTRACTS OF CRYOGENIC VAPOR SAMPLES

APPLICABILITY

This procedure applies to gas chromatography / mass spectrometry (GC/MS) analysis of methanol extracts from cryogenic vapor samples. Detected analytes may include gases, volatile organics and semivolatile organics. The methanol extraction procedure is part of the cryogenic vapor sampling methodology and is not reported here. The cryogenic sampling methodology may limit the possible analytes that can be trapped and extracted and hence detected by this procedure. For example, hydrogen, oxygen, and nitrogen will not be trapped by the cryogenic sampler and is not suitable for this analysis. The cryogenic sampling methodology is presently undergoing validation studies by Westinghouse Hanford Company (WHC).

DEFINITIONS

None

RESPONSIBLE STAFF

- COGNIZANT SCIENTIST
- ANALYST

PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 This method will be performed by the COGNIZANT SCIENTIST or a designated ANALYST.

1.2 Identification and quantitative analysis of many gases, volatile organics and semivolatile organics in methanol extracts of cryogenic vapor samples is possible by direct injection GC/MS analysis.

2.0 SUMMARY OF METHOD

2.1 The cryogenic methanol extract samples are received from Westinghouse Hanford Company (WHC). Samples are stored at 4°C prior to analysis.

Author / Date	Project Mgr. / Date	QAD Representative / Date
RB Lucke 10/2/91	10/2/91	B.O. BARNES 10/2/91
Technical Reviewer / Date	**Line Mgr. / Date**	**Other / Date**
J.A. Campbell 10/2/91	10/2/91	NA

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2.2 Since the samples are methanol extracts, extended holding times up to 6 months are allowed prior to analysis.

2.3 The samples are ran as is by direct injection GC/MS analysis. Quantitation may be done by the external standard method, internal standard method, or from the relative component abundances from a similar standard. All concentrations are reported in mg/L in methanol. In order to calculate concentrations in the vapor headspace, the cryo-sampling air volume and the methanol extract volume must be obtained from the cryo-sampling personnel at WHC. Purge and trap GC/MS can be used as an alternative method for volatile organic analysis.

3.0 INTERFERENCES

3.1 Samples may become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A field sample blank prepared from reagent methanol will be analyzed to check for such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with reagent methanol. Whenever a highly concentrated sample is encountered, it should be followed by an analysis of reagent methanol.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of methanol solvent blank that the entire analytical system is interference-free.

3.4 The injector and gas chromatography (GC) columns are subject to contamination; thereforr frequent bakeout and cleaning of the injector (replacement of liner) may be required.

4.0 APPARATUS AND MATERIALS

4.1 Balance: Analytical, capable of accurately weighing 0.0001 gm.

4.2 Vials: GC autosampler vials with teflon-lined crimped caps.

4.3 Gastight micro-syringe: 25 and 250 µL syringes.

4.4 GC/MS system

4.4.1 Gas Chromatograph: Temperature programmable GC suitable for on-column, split, and splitless injection. This includes accessories such as syringes, gases, and various capillary columns.

4.4.2 Columns: A capillary GC column suitable for both volatile and semivolatile organic analysis. A capillary DB1 column , 30 m x 0.32 mm i.d. x 5 µm film thickness (J & W Scientific) has proven to perform well.

4.4.3 Mass Spectrometer: Suitable for 70eV electron impact, and mass scan range from 10 to 500 m/z. Also must handle GC flow rates up to 2 mL/min to allow for optimal flow using a 0.32 mm i.d. capillary column.

4.4.4 Data system: A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Software must be available with a EPA / NIH library database of over 50,000 components' spectra and be capable of searching a sample spectra by reverse search algorithm.

5.0 REAGENTS

5.1 Methanol: HPLC grade or equivalent.

5.2 Stock standard solutions: stock standard solutions can be purchased as certified solutions or can be prepared from pure standard materials.

5.2.1 Place about 23 ml of methanol into a 25.0 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered , for about 5 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.2.2 Add the assayed standard material to the flask then reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in mg/L from the net gain in weight. Commercially prepared standards may be used at any concentration if they are certified by the manufacturer.

5.2.3 Transfer the stock standard solution into multiple Teflon-sealed screw-cap vials. Store with no headspace at -10°C to -20°C and protect from light.

5.2.4 Secondary dilution standards: Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.5 Example of standard solutions

5.2.5.1 Water and Ammonia Standard: Prepare a working standard containing water and ammonia as described in paragraphs 5.2.1 and 5.2.2.

5.2.5.2 Volatile and Semivolatile Standard: Prepare a standard mixture containing acetone, 1-butanol, benzene, normal paraffin hydrocarbon (NPH), and tributylphosphate (TBP) as described in paragraphs 5.2.1 and 5.2.2.

6. CALIBRATION

6.1 Internal Standard Method

6.1.1 Use an appropriate standard mixture that represents a volatile organic and a semivolatile organic but is not present in the sample. Deuterated standards such as d_6-benzene and d_{10} naphthalene are good examples.

6.1.2 Prepare a spiking solution containing each of the internal standards using the procedures described in paragraphs 5.2.1 and 5.2.2. Add equal aliquots of this standard to the samples and calibration standards.

6.1.3 Analyze each calibration standard and tabulate the area response of the characteristic ions against concentration for each compound and internal standard and calculate relative response factors (RRF) for each compound using Equation 1.

Equation 1: $RRF = [A_x/A_{is}] \times [C_{is}/C_x]$

Where:

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

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the internal standard.

C_x = Concentration of the compound to be measured.

6.2 External Standard Method

6.2.1 Analyze each calibration standard and tabulate the area response of the characteristic ions against concentration for each compound and calculate the response factors (RF) for each compound using Equation 2.

Equation 2: $RF = A_x/C_x$

7.0 SAMPLE ANALYSIS

7.1 Gas Analysis

7.1.1 Recommended operating conditions for the GC/MS: DB1, 30 m x 0.32 mm i.d. x 5 µm film thickness (J&W film thickness) with helium carrier gas at a flow rate of 2 mL/min. Column temperature isothermal at 40° C. Injection technique may be done by splittless, split, or on-column. If high concentrations of volatile and semivolatiles are present in the sample, it will be necessary to oven program the oven to elute off these analytes prior to the next sample injection.

7.1.2 Calibrate the system daily before and after each sample analyses set.

7.1.3 Analyze standards and samples by direct injecting 1 to 3 µL into the GC/MS. Recommended mass spectrometer conditions are 10 - 80 m/z, and scan time to give at least 5 scans per peak and not to exceed 2 seconds per scan. The MS electron energy must be at 70 electron volts (nominal).

7.2 Volatile and Semivolatile Analysis:

7.2.1 Recommended operating conditions for the GC/MS: Capillary DB1 column, 30 m x 0.32 mm i.d. x 5 µm film thickness (J&W film thickness) with helium carrier gas at a flow rate of 2 mL/min. Recommended oven temperature profile consist of linear oven temperature program from 40°C to 260°C. Injection technique may be done by splitless, split, or on-column.

7.2.2 Calibrate the system daily before and after each sample analyses set.

7.2.3 Analyze standards and samples by direct injecting 1 to 3 µL into the GC/MS. Recommended mass spectrometer conditions are 35-300 m/z, and scan time to give at least 5 scans per peak and not to exceed 2 seconds per scan. The MS electron energy must be at 70 electron volts (nominal).

8.0 QUALITATIVE ANALYSIS

8.1 The compounds shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify positive identifications: (1) elution of the sample component at the same GC retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

8.2 A library search shall be executed for non calibrated components for the purpose of tentative identification. Also classical mass spectral interpretation of the mass spectra will be made to attempt a tentative identification.

8.3 If in the technical judgement of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e. unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

9. QUANTITATIVE ANALYSIS

9.1 Internal Standard Method

9.1.1 The relative response factor (RRF) from the daily standard analysis is used to calculate the concentration in the sample. Use the RRF in the equation below to calculate concentration:

Concentration: $mg/L = [A_x/A_{is}] \times [Is/RRF]$

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

A_{is} = Area of the characteristic ion for the specific internal standard.

Is = Amount of internal standard added in nanograms (ng)

9.2 External Standard

9.2.1 The response factor (RF) from the daily standard analysis is used to calculate the concentration in the sample. Use the RF in the equation below to calculate concentration:

Concentration: $mg/L = A_x / RF$

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

9.3 Semiquantitation

9.3.1 Semiquantitation is used to estimate the concentration of a tentatively identified compound or an unknown compound.

9.3.2 The RRF or the RF is obtained from the standard compound closest in retention time to the compound of interest. Use that RRF or RF in the equation below to calculate the semi-concentrarion:

Semi-concentration Internal Standard Method
$mg/L = [A_x/A_{is}] \times [Is/RRF]$

Semi-concentration External Standard Method
$mg/L = A_x / RF$

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

RRF = Relative response factor of closest standard
RF = Response factor of closes standard

10.0 QUALITY CONTROL

10.1 Before processing any samples, the analyst should demonstrate through the analysis of a method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of sample preparation an measurement.

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-340-1
Page 1 of 1

A. Document Number: PNL-ALO-340 Revision Number: 0
Document Title: SCREENING OF SEMIVOLATILES ORGANIC EXTRACTS
Document's Original Author: RW Stromatt

Effective Date of ICN: 4 / 8 / 91

Change Requested By: RW Stromatt

B. Action:

Replace Applicability Section with that attached.

Pen and ink corrections on original.

C. Effect of Change:

To meet 200-BP-1 requirements

D. Reason for Change/Description of Change

Reason for change - To meet 200-BP-1 client request

Description of change - See attached

E. Approval Signatures

(Please Sign and Date)

Type of Change: (Check (✓) one)

(X) Minor Change ( ) Major Change

~~QSER~~ Process Quality Department Concurrence: GK Gerbe Date: 3/21/91

Approval Authority: [signature] Date: 3/21/91

Other Approvals: R. M. Gillespan Date: 3/21/91

: _____ Date: / /

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-340, SCREENING OF SEMIVOLATILES ORGANIC EXTRACTS

APPLICABILITY

This procedure applies to the screening analysis of organic solvent extracts of water and solid (soil/sediment) samples to assist in determining if the low or medium level extraction procedure in the sample preparation method should be followed. The procedure requires use of a gas chromatograph (GC) with a fused silica capillary column and a flame ionization detector.

DEFINITIONS

None

RESPONSIBLE STAFF

Cognizant Staff
Analysts

PROCEDURE

See Attachment 1 for the detailed procedure for this analysis.

The instrumentation used in this analysis is the HP5890 with a flame ionization detector and autosampler. Data are recorded and processed with an electronic chromatographic peak integrator.

QUALITY CONTROL

This procedure is designed as a guide only and no analytical data result from this procedure. However, the standard preparation and GC calibration steps must be followed.

Follow Section 3.2, GC calibration standard, in Attachment 1.

Follow Section 4.0, GC calibration, in Attachment 1.

Author	Date	Project Mgr.	Date	QAD Representative	Date
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Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
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REFERENCES

USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, 2/88, pages D-28/SV through D-30/SV of Exhibit D.

1. Summary of Method

1.1 The solvent extracts of water and sediment/soil are screened on a gas chromatograph/flame ionization detector (GC/FID) using a fused silica capillary column (FSCC). The results of the screen will determine the concentration of extract taken for GC/MS analysis.

2. Apparatus and Materials

2.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

2.1.1 Above GC equipped with flame ionization detector.

2.1.2 GC column - 30 m x 0.32 mm, 1 micron film thickness, silicone coated, fused silica capillary column (J & W Scientific DB-5 or equivalent).

3. Reagents

3.1 Methylene chloride - pesticide residue analysis grade or equivalent.

3.2 GC calibration standard. Prepare a standard solution containing phenol, phenanthrene and di-n-octylphthalate.

3.2.1 Stock standard solutions (1.00 ug/uL)-Stock standard solutions can be prepared from pure standard materials or purchased solutions.

3.2.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality methylene chloride and dilute to volume in a 10 mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is assayed at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source and are traceable to EMSL/LV-supplied standards.

3.2.1.2 Transfer the stock standard solutions into Teflon sealed screw-cap bottles. Store at -10°C to -20°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Stock standard solutions must be replaced after six months or sooner if comparison with quality control

check samples indicates a problem. Standards prepared from gases or reactive compounds such as styrene must be replaced after two months, or sooner if comparison with quality control check samples indicates a problem.

3.2.2 Prepare a working standard mixture of the three compounds in methylene chloride. The concentration must be such that the volume injected equals 50 ng of each compound. The storage and stability requirements are the same as specified in 3.2.1.2.

4. GC Calibration

4.1 At the beginning of each 12 hour shift, inject the GC calibration standard. The following criteria must be:

4.1.1 Standardized for half scale response from 50 ng of phenanthrene.

4.1.2 Adequately separates phenol from the solvent front.

4.1.3 Minimum of quarter scale response for 50 ng of di-n-octylphthalate.

5. GC/FID Screening

5.1 Suggested GC operating conditions:

Initial Column Temperature Hold - 50°C for 4 minutes

Column Temperature Program - 50 - 280°C at 8 degrees/min.

Final Column Temperature Hold - 280°C for 8 minutes

Injector - Grob-type, splitless

Sample Volume - 1 uL - 2 uL

Carrier Gas - Helium at 30 cm^3/sec

5.2 Inject the GC calibration standard and ensure the criteria specified in 4. are met before injecting samples. Estimate the response for 10 ng of phenanthrene.

5.3 Inject the appropriate extracts from Section II, including blanks.

6. Interpretation of Chromatograms

6.1 Water

6.1.1 If no sample peaks are detected, or all are less than full scale deflection, the undiluted extract is analyzed on GC/MS.

6.1.2 If any sample peaks are greater than full scale deflection, calculate the dilution necessary to reduce the major peaks to between half and full scale deflection. Use this dilution factor to dilute the extract for GC/MS analysis.

6.2 Soil/Sediment

6.2.1 If no sample peaks from the extract (from low or medium level preparation) are detected, or all are less than 10% full scale deflection, the sample must be prepared by the low level protocol, Section II, Part C, paragraph 2.

6.2.2 Peaks are detected at greater than 10% full scale deflection and less than or equal to full scale deflection.

6.2.2.1 If the screen is from the medium level extract, proceed with GC/MS analysis of this extract with appropriate dilution if necessary.

6.2.2.2 If screen is from the low level extract, discard extract and prepare sample by medium level method for GC/MS analysis.

6.2.3 Peaks are detected at greater than full scale deflection:

6.2.3.1 If the screen is from the medium level preparation, calculate the dilution necessary to reduce the major peaks to between half and full scale deflection. Use this dilution factor to dilute the extract. This dilution is analyzed by GC/MS for extractable organics.

6.2.3.2 If the screen is from the low level preparation, discard the extract and prepare a sample by the medium level method for GC/MS analysis.

7. <u>GC/MS Analysis</u>

7.1 Use the information from 6. to perform the GC/MS analysis of extractables in Section IV, GC/MS Analysis of Semivolatiles, paragraph 1.

APPLICABILITY

This procedure applies to the screening analysis of organic solvent extracts of water and solid (soil/sediment) samples prior to the GC/MS analysis for semivolatile organic compounds, method PNL-ALO-345. The screen is used to assist in determining if the low or medium level extraction procedure in the sample preparation method should be followed. The procedure requires use of a gas chromatograph (GC) with a fused silica capillary column and a flame ionization detector.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-341, GEL PERMEATION CHROMATOGRAPHY SAMPLE EXTRACT CLEANUP

APPLICABILITY

This procedure describes the gel permeation chromatography (GPC) cleanup of sample extracts obtained form the Procedure for Extraction of Single Shell Tank Samples For the Analysis of Semivolatile Organic Compounds. The use of GPC cleanup is recommended for soil/sediment extracts, in particular for the low level samples. This procedure is the USEPA Contract Laboratory Program Statement of Work, 2/88.

DEFINITIONS

None

RESPONSIBLE STAFF

Cognizant Scientists
Analysts

PROCEDURE

1.0 GPC Cleanup Device

1.1 Automated System

a) Gel permeation chromatograph Analytical Biochemical Labs, Inc. GPC Autoprep 1002 or equivalent including:
b) 25 mm ID x 600 - 700 mm glass column packed with 70 g of Bio-Beads SX-3.
c) Syringe, 10 ml with Luer-Lock fitting.
d) Syringe filter holder and filters - stainless steel and TFE, Gelman 4310 or equivalent.

1.2 Manual system assembled from parts. (Wise, R.H., Bishop, D.F., Williams, R.T., and Austern, B.M. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges" U.S. EPA, Municipal Environmental Research Laboratory, Cincinnati, OH 45268)

a) 25 mm ID x 600 - 700 mm heavy wall glass column packed with 70 g of BIO-Beads SX-3.

Author	Date	Project Mgr.	Date	QAD Representative	Date
R.W. Thomas	7/28/89			S L English	7-28-89
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
T. L. Hoppe	7-28-89	Walter C. Thomas	7/28/89		

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b) Pump: Altex Scientific, Model No. 1001A, semipreparative, solvent metering system. Pump capacity - 28 ml/min.

c) Detector: Altex Scientific, Model No. 153, with 254 nm UV source and 8-ul semi-preparative flowcells (2 mm pathlengths)

d) Microprocessor/controller: Altex Scientific, Model No. 420, Microprocessor System Controller, with extended memory.

e) Injector: Altex Scientific, Catalog No. 201-56, sample injection valve, Tefzel, with 10 ml sample loop.

f) Recorder: Linear Instruments, Model No. 385, 10-inch recorder.

g) Effluent Switching Valve: Teflon slider valve, 3-way with 0.060" ports.

h) Supplemental Pressure Gauge with connecting Tee: U.S. Gauge, 0-200 psi, stainless steel. Installed as a "downstream" monitoring device between column and detector. Flow rate was typically 5 ml/min. of methylene chloride. Recorder chart speed was 0.50 cm/min.

2.0 GPC Calibration Solutions

2.1 Corn oil - 200 mg/ml in methylene chloride.

2.2 Bis(2-ethylhexylphthalate) and pentachlorophenol 4.0 mg/ml in methylene chloride.

3.0 Extract Cleanup

3.1 GPC Setup and Calibration

a) Packing the column - Place 70 g of Bio Beads SX-3 in a 400 ml beaker. Cover the beads with methylene chloride; allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to top, at 5.0 ml/min. After approximately 1 hour, adjust the pressure on the column to 7 to 10 psi and pump an additional 4 hours to remove air from the column. Adjust the column pressure periodically as required to maintain 7 to 10 psi.

b) Calibration of the column - Load 5 ml of the corn oil solution into sample loop No. 1 and 5 ml of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10 ml fraction (i.e., change fraction at 2-minute intervals) for 36 minutes. Inject the phthalate-phenol solution and collect 15 ml fractions for 60 minutes. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID on the DB-5 capillary column, a UV spectrophotometer or a GC/MS system. Plot the concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose a "dump time" which allows >85% removal of the corn oil and ≥85% recovery of the bis(2-ethylhexyl)-phthalate. Choose the "collect time" to extend at lease 10 minutes after the elution of pentachlorophenol. Wash the column at lease 15 minutes between samples. Typical parameters selected are: Dump time, 30 minutes (150 ml), collect time, 36 minutes (180 ml) and wash time, 15 minutes (75 ml). The column can also be calibrated by the use of a 254 mm UV detector in place of gravimetric and GC analyses of fractions. Measure the peak areas at various elution times to determine appropriate fractions.

The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. System calibration usually remains constant over this period of time if column flowrate remains constant.

3.2 GPC Extract Cleanup

Prefilter or load all extracts via the filter holder to avoid particulates that might stop the flow. Load one 5.0 ml aliquot of the extract onto the GPC column. Do not apply excessive pressure when loading the GPC. Purge the sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carry-over. Process the extracts using he dump, collect and wash parameters determined from the calibration and collect the cleaned extracts in 400 ml beakers tightly covered with aluminum foil. The phthalate-phenol calibration solution shall be taken through the cleanup cycle with each set of 23 extract loaded into the GPC. The recovery for each compound must be ≥85%. This must be determined on a

GC/FID, using a DB-5 capillary column, a UV recording spectrophotometer or a CC/MS system. A copy of the printouts of standard and check solution are required as deliverables with each case. Show % recovery on the copy.

3.3 Concentrate the extract as per paragraphs 2.5.7 and 2.5.8

4.0 QUALITY CONTROL

Follow conditions specified in the GPC calibration and cleanup.

5.0 REFERENCES

USEPA Contract Laboratory Program Statement of Work for Organic Analysis Multi-Media, Multi-Concentration, 2/88, pages D-18/SV through D-20/SV and D-23/SV through D-24/SV.

TITLE: PNL-ALO-344, PROCEDURE FOR PREPARATION OF SAMPLES FOR GC/MS ANALYSIS FOR SEMIVOLATILE ORGANIC COMPOUNDS

APPLICABILITY

This procedure describes the method for the extraction of liquid and soil/sediment samples and subsequent preparation of the extract for the GC/MS analysis of semivolatile organic compounds per Procedure PNL-ALO-345. Also described in this procedure is the optional gel permeation chromatography (GPC) cleanup of extracts prior to the GC/MS analysis. This procedure may be used to support work performed in compliance with EPA Contract Laboratory Program (CLP) or other programs/projects as elected. This procedure is taken from the USEPA CLP Statement of Work for Organic Analysis, 2/88.

DEFINITIONS

N/A

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

QUALITY CONTROL

Sample preparation steps that support the quality control (QC) requirements for the GC/MS analysis, Procedure PNL-ALO-345, are included in the procedure.

SAMPLE STORAGE AND HOLDING TIME

- The sample must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until extraction and analysis. Extracts and unused samples are maintained protected from light and refrigerated at 4°C (±2°C) until returned to the client, or discarded, as specified by the client.

- If separatory funnel or sonication procedures are employed for extractions for semivolatile organics analyses, extraction of water samples shall be completed within five days of sample receipt, and extraction of soil/sediment samples shall be completed within 10 days of sample receipt. If continuous liquid-liquid extraction procedures are employed, extraction of water samples shall be started within five

Author / Date	Project Mgr. / Date	QP Representative / Date
RW Stromatt 12-23-92	TY Hosaka 3/11/93	TL Ehlert 3/11/93
Technical Reviewer / Date	**Line Mgr. / Date**	**Other / Date**
EW Hoppe 3/11/93	AG King 3/11/93	

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of sample receipt. Extracts of either water or soil/sediment samples must be analyzed within forty days following extraction.

PROCEDURE

1.0 SAMPLE PREPARATION FOR EXTRACTABLE SEMI-VOLATILES (BNA) IN WATER

1.1 Summary of Method

A measured volume of sample, approximately one liter, is serially extracted with methylene chloride at a pH greater than 11 and again at pH less than 2, using a separatory funnel or a continuous extractor. The methylene chloride extracts are dried and concentrated separately to a volume of 1 mL. Radioactive samples may be less than 1 L in volume because of sample availability and dose rate.

1.2 Interferences/Tolerance

1.2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware, that lead to discrete artifacts and/or elevated baselines in the total ion current profiles (TICPs). All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

1.2.2 Unless otherwise stated tolerances for all values given within this method are within the first, non-zero, significant integer, including the number 10, that is specified. For example, 5 mL implies accuracy to within ±1 mL, while 5.0 mL implies accuracy within ±0.1 mL. If 100 mL is specified, it implies accuracy to ±1 mL.

When preparing samples and standards, and making standard spike addition, the volumes specified shall be measured to that value using the specified or appropriate measuring device. For example, if 1 L water sample is specified to be measured in a 1 L graduated cylinder, the water sample is added to the 1000 mL mark: if 7.5 µL is specified, a 10 µL gas tight syringe is filled to the 7.5 µL mark: if 30 µL is specified, a 50 µL gas tight syringe is filled to the 30 µL mark. Manufacturer tolerances are acceptable for the specified volumetric measurements in this procedure.

1.3 Apparatus and Materials

1.3.1 Glassware (Brand names and catalog numbers are included for illustration purposes only).

1.3.1.1 Separatory funnel, 2,000 mL, with Teflon stopcock.

1.3.1.2 Drying column, 19 mm ID chromatographic column with coarse frit. Substitution of a small pad of Pyrex glass wool for the frit will prevent cross contamination of sample extracts, and is recommended.

1.3.1.3 Concentrator tube, Kuderna-Danish (K-D), 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

1.3.1.4 Evaporative flask, K-D, 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

1.3.1.5 Snyder column, K-D, three-ball macro (Kontes K-503000-0121 or equivalent).

1.3.1.6 Snyder column, K-D, two-ball micro (Kontes K569001-0219 or equivalent).

1.3.1.7 Vials, amber glass, 2 mL capacity with Teflon-lined screw cap.

1.3.1.8 Continuous liquid-liquid extractors, equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor-Ace Glass Company, Vineland, NJ P/N 6841-10 or equivalent).

1.3.2 Silicon carbide boiling chips, approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

1.3.3 Water bath, heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

1.3.4 Balance, analytical, capable of accurately weighing ±0.0001 g.

1.3.5 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc., South Berlin, MA (or equivalent) is suitable.

1.4 Reagents

1.4.1 Reagent water, reagent water is defined as a water in which an interferant is not observed at or above the Contract Required Quantitation Limit (CRQL) of each parameter of interest.

1.4.2 Sodium hydroxide solution (10 N), dissolve 40 g reagent grade NaOH in reagent water and dilute to 100 mL.

1.4.3 Sodium thiosulfate, granular, reagent grade.

1.4.4 Sulfuric acid solution (1+1), slowly add 50 mL of reagent grade H_2SO_4 (sp gr.1.84) to 50 mL of reagent water.

1.4.5 Acetone, methanol, and methylene chloride; pesticide quality or equivalent.

1.4.6 Sodium sulfate, (ACS) powdered, anhydrous. Purify by heating at 400°C for four hours in a shallow tray, cool in a desiccator and store in a glass bottle. Baker anhydrous powder, catalog #73898 or equivalent.

1.4.7 Surrogate standard spiking solution.

1.4.7.1 Surrogate standards are added to all samples and calibration solutions; the compounds specified for this purpose are phenol-d_5; 2,4,6 tribromophenol; 2-fluorophenol; nitrobenzene-d_5; terphenyl-d_{14} and 2-fluorobiphenyl. Two additional surrogates, one base/neutral and one acid, may be added.

1.4.7.2 Prepare a surrogate standard spiking solution that contains the base/neutral compounds at a concentration of 100 µg/mL, and the acid compounds at 200 µg/mL. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner if comparison with QC check samples indicates a problem. The acid and base/neutral surrogates may be in two separate spiking stock solutions.

1.4.8 BNA Matrix standard spiking solution. The matrix spike solution consists of:

Base/Neutrals	Acids
1,2,4-trichlorobenzene	pentachlorophenol
acenaphthene	phenol
2,4-dinitrotoluene	2-chlorophenol
pyrene	4-chloro-3-methylphenol
N-nitroso-di-n-propylamine	4-nitrophenol
1,4-dichlorobenzene	

Prepare a spiking solution that contains each of the base/neutral compounds above at 100 μg/1.0 mL in methanol and the acid compounds at 200 μg/1.0 mL in methanol. Analyze duplicate aliquots of a sample spiked with BNA matrix spiking solution. The acid and base/neutral surrogates may be in two separate spiking stock solutions.

1.5 Sample Extraction - Separatory Funnel

1.5.1 Samples may be extracted using separatory funnel techniques. If emulsions prevent acceptable solvent recovery with separatory funnel extraction, continuous extraction (section 1.6) may be used. Continuous extraction is also advantageous to reduce analyst contact with radioactive samples.

1.5.2 Using a 1 L graduated cylinder, measure out a 1 L sample aliquot and place it into a 2 L separatory funnel. Pipet 1.0 mL surrogate standard spiking solution, or 1.0 mL each of the acid and base/neutral surrogate spiking solutions, into the separatory funnel and mix well. Check the pH of the sample with wide range pH paper and adjust to pH>11 with 10 N sodium hydroxide. Add 1.0 mL of BNA matrix spiking solution, or 1.0 mL each of the acid and base/neutral matrix spiking solutions, to each of two 1 L portions from the sample selected for spiking. If samples are extracted in hot cells, 100 mL separatory funnels are used. Samples with volumes as much as 1 L are rarely available for radioactive samples.

1.5.3 Add 60 mL methylene chloride to the separatory funnel and extract the sample by shaking the funnel for two minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume 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 methylene chloride extract in a 250 mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent and emulsion into the extraction chamber of a continuous extractor. Proceed as described in paragraph 1.6.3.

1.5.4 Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

1.5.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid (1 + 1). Serially extract three times with 60 mL aliquots of methylene chloride, as per paragraph 1.5.3. Collect and combine the extracts in a 250 mL Erlenmeyer flask and label the combined extract as the acid fraction.

1.5.6 Assemble a K-D concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D, if equivalency is demonstrated for all extractable organics shown in the Target Compound List table in PNL-ALO-345.

1.5.7 Transfer the individual base/neutral and acid fractions by pouring extracts through separate drying columns containing about 10 cm of anhydrous granular sodium sulfate, and collect the extracts in the separate K-D concentrators. Alternatively, pour the extracts through the conical funnels mounted on the K-D concentrator with at least 5 cm depth of the sodium sulfate. Rinse the Erlenmeyer flasks and columns with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

1.5.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding an apparent volume of 1 mL methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80 to 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 15 minutes. A longer period of time may be required if the temperature is maintained 90°C or less and if the concentration process is performed in a high air flow radiochemistry hood. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for a least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5 mL syringe is recommended for this operation.

1.5.9 Micro-Snyder column technique - Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro-Snyder column. Pre-wet the Snyder column by adding an apparent volume of 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. A longer period of time may be required if the temperature is maintained 90°C or less and if the concentration process is performed in a high air flow radiochemistry hood. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for a least 10 minutes while cooling. Remove the Snyder column and rinse its flask and its lower joint into the concentrator tube with an apparent volume of 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with methylene chloride. If GC/MS analysis will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extracts will be stored longer than two days, they should be transferred to individual Teflon-sealed screw cap bottles and labeled base/neutral or acid fraction, as appropriate.

1.5.10 Nitrogen blowdown technique (taken from ASTM Method D3086).

The following method may be used for final concentration, instead of the procedure outlined in paragraph 1.5.9. Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to just below 1 mL using a gentle stream of clean, dry nitrogen filtered through a column of activated carbon. **CAUTION:** New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of the tube must be rinsed down several times with methylene chloride during the operation and the final volume brought to 1.0 mL with methylene chloride. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

1.6 Sample Extraction - Continuous Liquid-Liquid Extractor

1.6.1 Check the pH of the sample with wide-range pH paper and adjust to pH>11 with 10 N sodium hydroxide. Transfer a 1 L sample aliquot to the continuous extractor; using a pipet, add 1 mL of surrogate standard spiking solution or 1 mL each of the acid and base/neutral surrogate spiking solutions and mix well. Sample volumes of 1 L may not be available or practical for radioactive samples. Lesser volumes may be required because of sample dose rate. Consult cognizant scientist for direction.

1.6.2 Add 500 mL of methylene chloride to the distilling flask. Add sufficient reagent water to ensure proper operation and extract for 18 hours. Allow to cool, then detach the boiling flask and dry. Concentrate the extract as in paragraphs 1.5.6 through 1.5.8. Hold the concentrated extract for combining with the acid extract (see paragraph 1.6.4).

1.6.3 Add 500 mL of methylene chloride to a clean distilling flask and attach it to the continuous extractor. Carefully adjust the pH of the aqueous phase to less than 2 using sulfuric acid (1 + 1). Extract for 18 hours. Dry and concentrate the extract as described in paragraphs 1.5.6 through 1.5.8. Hold the concentrated extract and label as the acid extract.

1.6.3.1 If the base/neutral and/or acid extracts cannot be concentrated to a final volume of 1 mL, dilute the more concentrated extract to the final volume of the least concentrated extract.

1.7 The samples extracts are ready for GC/MS analysis. Proceed to Procedure PNL-ALO-345. If high concentrations are suspected (e.g.,

highly colored extracts), the optional GC/FID screen in Procedure PNL-ALO-340 is recommended.

2.0 PROTOCOLS FOR SOIL/SEDIMENT

It is mandatory that all soil/sediment samples be characterized as to concentration level so that the appropriate analytical protocol is chosen to ensure proper quantitation limits for the sample. Note that the terms "low level" and "medium level" are not used here as a judgement of degree of contamination but rather as description of the concentration ranges that are encompassed by the "low" and "medium" level procedures.

The laboratory is a liberty to determine the method of characterization. The following two screening methods may be used for soil/sediment sample characterization:

- Screen an aliquot from the "low level" 30 g extract or an aliquot from the "medium level" 1 g extract.
- Screen using the GC/FID as the screening instrument (method PNL-ALO-340).

The concentration ranges covered, may be considered to be approximately 330 µg/kg - 20,000 µg/kg for the low level analysis and >20,000 µg/kg for medium level analysis for BNA extractables. For soils only, the extract for pesticide/PCB analysis may be prepared from an aliquot of the extract for semi-volatile, or in a separate extraction procedure. If it is prepared from the semi-volatile extract, refer to Procedure PNL-ALO-347 for the procedures for extraction of pesticides/PCBs.

Screen from the Medium Level Method

Take 5.0 mL from the 10.0 mL total extract and concentrate to 1.0 mL and screen. If the sample concentration is >20,00 µg/kg proceed with GC/MS analysis of the organics. If the sample concentration is <20,000 µg/kg discard the medium level extract and follow the low level method.

Screen from low Level Method

Take 5.0 mL from the 300 mL (approximate) total extract from the 30 g sample and concentrate to 1.0 mL and screen. If the concentration is >20,000 µg/kg in the original sample, discard the 30 g extract and follow the medium level methods for organics, using medium level surrogates. If the sample concentration is <20,000 µg/kg, proceed with concentration and the remainder of the low level method.

2.1 Medium Level Preparation for Screening & Analysis of Semivolatile (BNA)

2.1.1 Scope and Application

This procedure is designed for the preparation of sediment/soil samples which may contain organic chemicals at a level greater than 20,000 µg/kg.

2.1.1.1 The extracts and sample aliquots prepared using this method are screened by GC/MS or FID, using capillary columns for base/neutral and acid priority pollutants, and related organic chemicals. The results of these screens will determine whether sufficient quantities of pollutants are present to warrant analysis by low or medium protocol.

2.1.1.2 If the screenings indicate no detectable pollutants at the lower limits of quantitation, the sample should be prepared by the low level protocol in Section 2.2.

2.1.2 Summary of Method

2.1.2.1 Approximately 1 g portions of sediment/soil are transferred to vials and extracted with methylene chloride. The methylene chloride extract is screened for extractable organics by GC/FID or GC/MS.

2.1.2.2 If organic compounds are detected by the screen, the methylene chloride extract is analyzed by GC/MS for extractable organics.

2.1.2.3 If no organic compounds are detected by the medium level screen, then a low level sample preparation is required.

2.1.3 Interferences

2.1.3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

2.1.4 Limitations

2.1.4.1 The procedure is designed to allow quantitation limits for screening purposes as low as 20,000 μg/kg for extractable organics. For analysis purposes, the quantitation limits are 20,000 μg/kg for extractable organics. If peaks are present based on the GC/FID screen, the sample is determined to require a medium level analysis by GC/MS. Some samples may contain high concentrations of chemicals that interfere with the analysis of other components at lower levels; the quantitation limits in those cases may be significantly higher.

2.1.4.2 These extraction and preparation procedures were developed for rapid and safe handling of high concentration hazardous waste samples. The design of the methods thus does not stress efficient recoveries or low limits of quantitation of all components. Rather, the procedures were designed to screen at moderate recovery and sufficient sensitivity, a broad spectrum of organic chemicals. The results of the analyses thus may reflect only a minimum of the amount actually present in some samples.

2.1.5 Reagents

2.1.5.1 Sodium Sulfate, anhydrous powdered reagent grade, heated at 400°C for four hours, cooled in a desiccator, and stored in a glass bottle, Baker anhydrous powder, catalog #73898 or equivalent.

2.1.5.2 Methylene chloride, pesticide residue analysis grade or equivalent.

2.1.5.3 Methanol, pesticide residue analysis grade or equivalent.

2.1.5.4 Acetone, pesticide residue analysis grade or equivalent.

2.1.5.5 Base/Neutral and Acid Surrogate Standard Spiking Solution.

The compounds specified are phenol-d_5, 2,4,6-tribromophenol, 2-fluorophenol, nitrobenzene-d_5, terphenyl-d_{14} and 2-fluorobiphenol. Prepare a solution containing these compounds for base/neutral surrogates at a concentration of 100 μg/1.0 mL in methanol, and a second solution for acid surrogate standards at a concentration of 200 μg/1.0 mL in methanol. Store the

spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with QC check samples indicates a problem.

2.1.5.6 Base/Neutral and Acid Matrix Standard Spiking solution.

Prepare a spiking solution in methanol that contains the following compounds at a concentration of 100 μg/1.0 mL for base/neutrals and 200 μg/1.0 mL for acids. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with QC check samples indicates a problem. The acid and base/neutral compounds may be in two separate spiking stock solutions.

Base Neutrals	Acids
1,2,4-trichlorobenzene	pentachlorophenol
acenaphthene	phenol
2,4-dinitrotoluene	2-chlorophenol
pyrene	4-chloro-3-methylphenol
N-nitroso-di-n-propylamine	4-nitrophenol
1,4-dichlorobenzene	

2.1.6 Equipment

2.1.6.1 Glass scintillation vials, at least 20 mL, with screw cap and Teflon liner, or equivalent pre-cleaned vial.

2.1.6.2 Spatula, stainless steel or Teflon.

2.1.6.3 Balance capable of weighing 100 g to ±0.01 g.

2.1.6.4 Vials and caps, 2 mL for GC auto sampler.

2.1.6.5 Disposable pipets, Pasteur.

2.1.6.6 15 mL concentrator tubes.

2.1.6.7 Ultrasonic cell disrupter, Heat Systems Ultrasonics, Inc., Model W-385 SONICATOR (475 Watt with pulsing capability, No. 200 1/2 in. tapped disrupter horn plus No. 207 3/4 in. tapped disrupter horn, and No. 419 1/8 in. standard tapered MICROTIP probe), or equivalent device with a minimum of 375 Watt output capability.

NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the MICROTIP probe must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

2.1.6.8 Sonabox acoustic enclosure, recommended with above disrupters for decreasing cavitation sound.

2.1.6.9 Test tube rack.

2.1.6.10 Oven, drying.

2.1.6.11 Desiccator.

2.1.6.12 Crucibles, porcelain.

2.1.6.13 Glass wool, rinsed with methylene chloride.

2.1.7 Medium Level Sample Preparation.

2.1.7.1 Transfer the sample container into a fume hood. Open the sample vial. Decant and discard any water layer and then mix the sample. Transfer approximately 1 g (record weight to at least the nearest 0.1 g) of sample to a vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

2.1.7.1.1 Transfer 50 g of soil/sediment to 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample with glass electrode and pH meter while stirring (combined methods PNL-ALO-120 and PNL-ALO-225). Because of sample availability limits and radioactivity it may be necessary to use proportionate smaller quantities. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the cognizant scientist for instructions on how to handle the sample. Document the instructions in the Case Narrative. Discard this portion of sample.

2.1.7.2 Immediately after weighing the sample for extraction, weigh 5-10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment. This step may be

performed in the hot cells, or as part of another procedure with the data being transferred to the organic data package for use in sample calculations.

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

2.1.7.3 Add 2.0 g of anhydrous powdered sodium sulfate to sample in the vial from paragraph 2.1.7.1 and mix well.

2.1.7.4 Surrogate standards are added to all samples, spikes, and blanks. Add 1.0 mL of surrogate spiking solution to sample mixture. The acid and base/neutral spikes may be added as separate 1.0 mL spiking solutions.

2.1.7.5 Add 1.0 mL of matrix standard spiking solution to each of two 1 g portions from the sample chosen for spiking. The acid and base/neutral spikes may be added in separate 1.0 mL spiking solutions.

2.1.7.6 Immediately add 9.0 mL of methylene chloride to the sample, or 8.0 mL if the 1-mL acid, and base/neutral spikes are added separately. The total volume of the methylene chloride plus spikes is 10 mL. Disrupt the sample with the 1/8 inch tapered MICROTIP ultrasonic probe for 2 minutes at output control setting 5, in continuous mode. (If using a sonicator other than Models W-375 or W-385, contact the Project Officer for appropriate output settings.) Before extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or very carefully with the tip of the unenergized probe.

2.1.7.6.1 Add only 8.0 mL of methylene chloride to the matrix spike samples to achieve a final volume of 10 mL, or add 6.0 mL if each of the acid and base neutral surrogate and matrix spikes are added separately as 1-mL spikes. The total volume of the methylene chloride plus spikes is 10-mL.

2.1.7.7 Loosely pack disposable Pasteur pipets with 2-3 cm glass wool plugs. Filter the extract through the glass wool and collect 5.0 mL in a concentrator tube.

2.1.7.8 Concentrate the extract to 1.0 mL by the nitrogen blowdown technique described in paragraph 2.2.7.3, or the micro-Snyder column technique (see Section 1.5.9).

2.1.7.9 Transfer the concentrate to an autosampler vial for GC/FID or GC/MS capillary column screening. If the concentrate is screened, the quantitation limits should be approximately 20,000 μg/kg.

2.1.7.10 Proceed to PNL-ALO-340 for screening, if needed.

2.2 Low Level Preparation for Screening & Analysis of Semi-volatiles (BNA)

2.2.1 Summary of Method

A 30 gram portion of sediment is mixed with anhydrous powdered sodium sulfate and extracted with 1:1 methylene chloride/acetone using an ultrasonic probe. If the optional low level screen is used, a portion of this dilute extract is concentrated fivefold and is screened by GC/FID or GC/MS. If peaks are present at greater than 20,000 μg/kg, discard the extract and prepare the sample by the medium level method. If no peaks are present at greater than 20,000 μg/kg, the extract is concentrated. An optional gel permeation column cleanup (section 2.2.6) may be used before analysis. Other cleanup methods may be required depending on the sample. The cognizant scientist shall be contacted for direction.

2.2.2 Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion-current profiles (TICPs).

All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

2.2.3 Apparatus and Materials

2.2.3.1 Apparatus for determining percent moisture

2.2.3.1.1 Oven, drying

2.2.3.1.2 Desiccator

2.2.3.1.3 Crucibles, porcelain

2.2.3.2 Disposable Pasteur glass pipets, 1 mL

2.2.3.3 Ultrasonic cell disrupter, Heat Systems, Ultrasonics, Inc. Model 385 SONICATOR (475 Watt with pulsing capability, No. 305 3/4 in. tapped high gain "Q" disrupter horn or No. 208 3/4 in. standard solid disrupter horn), or equivalent device with a minimum of 375 Watt output capability.

NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

2.2.3.3.1 Sonabox acoustic enclosure - recommended with above disrupters for decreasing cavitation sound.

2.2.3.4 Centrifuge bottles, 200 mL, heavy walled, Corning 1261 or equivalent.

2.2.3.5 Vacuum filtration apparatus

2.2.3.5.1 Funnel, fluted, 10 cm.

2.2.3.5.2 Filter paper, Whatman No. 41 or equivalent.

2.2.3.6 K-D apparatus.

2.2.3.6.1 Concentrator tube, 10 mL, graduated (Kontes K-570040-1025 or equivalent).

2.2.3.6.2 Evaporative flask, 500 mL (Kontes K-570001-0500 or equivalent).

2.2.3.6.3 Snyder column, three-ball macro (Kontes K-503000-0121 or equivalent).

2.2.3.6.4 Snyder column, two-ball micro (Kontes K-569001-0219) or equivalent).

2.2.3.7 Silicon carbide boiling chips, approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

2.2.3.8 Water bath, heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

2.2.3.9 Balance, capable of accurately weighing ±0.01 g.

2.2.3.10 Vials and caps, 2 mL for GC auto sampler.

2.2.3.11 Balance, analytical, capable of accurately weighing ±0.0001 g.

2.2.3.12 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc., South Berlin, MA (or equivalent) is suitable.

2.2.3.13 GPC cleanup devise.

NOTE: GPC cleanup is highly recommended for all extracts for low level soils.

2.2.3.13.1 Automated systems

2.2.3.13.1.1 GPC Analytical Biochemical Laboratories, Inc. GCP Autoprep 1002 or equivalent including:

2.2.3.13.1.2 25 mm ID X 600, 700 mm glass column packed with 70 g of Bio-Beads SX-3.

2.2.3.13.1.3 Syringe, 10 mL with Luer-Lock fitting.

2.2.3.13.1.4 Syringe filter holder and filters, stainless steel and TFE, Gelman 4310 or equivalent.

2.2.3.13.2 Manual system assembled from parts. (Wise, R. H., Bishop, D. F., Williams, R. T. & Austern, B. M. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges" U.S. EPA, Municipal Environmental Research Laboratory, Cincinnati, Ohio 45268).

2.2.3.13.2.1 25 mm ID X 600, 700 mm heavy wall glass column packed with 70 g of BIO-Beads SX-3.

2.2.3.13.2.2 Pump, Altex Scientific, Model No. 1001A, or equivalent, semi-preparative, solvent metering system. Pump capacity, approximately 28 mL/min.

2.2.3.13.2.3 Detector, Altex Scientific, Model No. 153, or equivalent, with 254 nm UV source and 8 μL semi-preparative flowcells (2 mm pathlengths).

2.2.3.13.2.4 Microprocessor/controller, Altex Scientific, Model No. 420, or equivalent, Microprocessor System Controller, with extended memory.

2.2.3.13.2.5 Injector, Altex Scientific, Catalog No. 201-56, or equivalent, sample injection valve, Tefzel, with 10 mL sample loop.

2.2.3.13.2.6 Recorder, Linear Instruments, Model No. 385, or equivalent, 10 in. recorder.

2.2.3.13.2.7 Effluent Switching Valve, Teflon slider valve, 3-way with 0.060 in. ports.

2.2.3.13.2.8 Supplemental Pressure Gauge with connecting Tee, U.S. Gauge, 0-200 psi, stainless steel. Installed as a "downstream" monitoring device between column and detector.

Flow rate was typically 5 mL/min. of methylene chloride. Recorder chart speed was 0.50 cm/min.

2.2.3.14 Pyrex glass wool.

2.2.3.15 Pasteur pipets, disposable.

2.2.4 Reagents

2.2.4.1 Sodium Sulfate, anhydrous <u>powdered</u> reagent grade, heated at 400°C for four hours, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog #73898 or equivalent.

2.2.4.2 Methylene chloride, methanol, acetone, isooctane, 2-propanol and benzene pesticide quality or equivalent.

2.2.4.3 Reagent water, Reagent water is defined as a water in which an interferant is not observed at or above the CRQL of each parameter of interest.

2.2.4.4 GPC calibration solutions:

2.2.4.4.1 Corn oil, 200 mg/mL in methylene chloride.

2.2.4.4.2 Bis(2-ethylhexylphthalate) and pentachlorophenol 4.0 mg/mL in methylene chloride.

2.2.4.5 Sodium Sulfite, reagent grade.

2.2.4.6 Surrogate standard spiking solution.

2.2.4.6.1 Base/neutral and acid surrogate solution.

2.2.4.6.1.1 Surrogate standards are added to all samples, blanks, matrix spikes, matrix spike duplicates, and calibration solutions; the compounds specified for this purpose are phenol-d_5, 2,4,6-tribromophenol, 2-fluorophenol, nitrobenzene-d_5, terphenyl-d_{14} and 2-fluorobiphenyl. Two additional surrogates, one base/neutral and one acid may be added.

2.2.4.6.1.2 Prepare a surrogate standard spiking solution at a concentration of 100 µg/1.0 mL in methanol for base/neutral and one at 200 µg/1.0 mL for acids in methanol. Store the spiking solution at ±4°C (±2°C) in Teflon-sealed containers. The solutions must be replaced after 12 months, or sooner if comparison with quality control check samples indicate a problem.

2.2.4.7 Matrix standard spiking solutions.

2.2.4.7.1 Base/neutral and acid matrix spiking solution consists of:

Base/Neutrals (100 µg/1.0 mL)	Acids (200 µg/1.0 mL)
1,2,4-trichlorobenzene	pentachlorophenol
acenaphthene	phenol
2,4-dinitrotoluene	2-chlorophenol
pyrene	4-chloro-3-methylphenol
N-nitroso-di-n-propylamine	4-nitrophenol
1,4-dichlorobenzene	

Prepare a spiking solution that contains each of the above in methanol. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner if comparison with quality control check samples indicate a problem. The acid and base/neutral compounds may be in two separate spiking stock solutions.

Matrix spikes also serve as duplicates, therefore, add volume specified in Sample Extraction section to each of two 30 g portions from one sample chosen for spiking.

2.2.5 Low Level Sample Preparation

2.2.5.1 Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited sample. Discard any foreign objects such as sticks, leaves, and rocks.

2.2.5.1.1 Transfer 50 g of soil/sediment to 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample (combination of PNL-ALO-120 and PNL-ALO-225) with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the cognizant scientist for instructions on how to handle the sample. Document the instructions in the Case Narrative. Discard this portion of sample.

2.2.5.2 The following steps should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample to the nearest 0.1 g into a 200 mL centrifuge bottle and add 60 g of anhydrous powdered sodium sulfate. Mix well. The sample should have a sandy texture at this point. Immediately, add 100 mL of 1:1 methylene chloride - acetone to the sample, then add the surrogates according to paragraph 2.2.5.2.3.

2.2.5.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sediment into a tared crucible (the amount of sample may be less because of high radioactivity or limited availability). Determine the percent moisture (PNL-ALO-504) by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment. This step may be performed in the hot cells, or as part of another procedure with the data being transferred to the organic data package for use in sample calculations.

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \%\ \text{moisture}$$

2.2.5.2.2 Weigh out two 30 g (record weight to nearest 0.1 g) portions for use as matrix and matrix spike duplicates according to paragraph 2.2.5.2. When using GPC cleanup, add 2.0 mL of the base/neutral and acid matrix spike to each of two portions. When <u>not</u> using GPC cleanup, add 1.0 mL of base/neutral and acid matrix spike to each of the other two portions.

2.2.5.2.3 When using GPC, add 1.0 mL of base/neutral and acid surrogate standard to the sample. When not using GPC, add 0.5 mL of BNA surrogate standard to the sample.

2.2.5.3 Place the bottom surface of the tip of the 3/4 in. disrupter horn about 1/2 in. below the surface of the solvent but above the sediment layer.

2.2.5.4 Sonicate for 1 1/2 minutes with the W-385 (or 3 minutes with the W-375), using No. 208 3/4 in. standard disrupter horn with output control knob set at 10 (or No. 305 3/4 in. tapped high gain "Q" disrupter horn at 5) and mode switch on "1 sec. pulse" and % duty cycle knob set at 50%. Do NOT use MICROTIP probe. (If using a sonicator other than Models W-375 or W-385, contact the Cognizant Scientist for appropriate output settings.)

2.2.5.5 Decant and filter extracts through Whatman #41 filter paper using vacuum or gravity filtration or centrifuge and decant extraction solvent.

2.2.5.6 Repeat the extraction two more times with two additional 100 mL portions of 1:1 methylene chloride - acetone. Before each extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or very carefully with the tip of the probe. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the funnel and rinse with 1:1 methylene chloride - acetone.

2.2.5.6.1 If the sample is to be screened from the low level method, take 5.0 mL and concentrate to 1.0 mL following paragraph 2.2.7.2 or 2.2.7.3. Note that the sample volume in this case is 5.0 mL not 10.0 mL as given in paragraph 2.2.7.2. Screen the extract as per Procedure PNL-ALO-340, "Screening of Semivolatile Organic Extracts." Transfer the remainder of the 1 mL back to the total extract from paragraph 2.2.5.6 after GC/FID or GC/MS screening. (**CAUTION**: To minimize sample loss, autosamplers which pre-flush samples through the syringe should not be used.)

2.2.5.7 Transfer the extract to a K-D concentrator consisting of a 10 mL concentration tube and a 500 mL evaporative flask. Other concentration devices or techniques may be used if equivalency is demonstrated for all extractable compounds listed on page C-4 of Procedure PNL-ALO-345.

2.2.5.8 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding an apparent volume of 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 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 15 minutes. A longer period of time may be required if the temperature is maintained 90°C or less and if the concentration process is performed in a high air flow radiochemistry hood. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes, and make up to 10 mL volume with methylene chloride.

2.2.5.9 If GPC cleanup is not used proceed to paragraph 2.2.7.

2.2.6 Extract Cleanup

2.2.6.1 GPC Setup and Calibration

2.2.6.1.1 Packing the column - Place 70 g of Bio Beads SX-3 in a 400 mL beaker. Cover the beads with methylene chloride; allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to top, at 5.0 mL/min. After approximately 1 hour, adjust the pressure on the column to 7 to 10 psi and pump an additional 4 hours to remove air from the column. Adjust the column pressure periodically as required to maintain 7 to 10 psi.

2.2.6.1.2 Calibration of the column - Load 5 mL of the corn oil solution into sample loop No. 1 and 5 mL of the phthalatephenol solution into loop No. 2. Inject the corn oil and collect 10 mL fraction (i.e., change fraction at 2 minute intervals) for 36 minutes. Inject the phthalate-phenol solution and collect 15 mL fractions for 60 minutes. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID on the DB-5 capillary column, a UV

spectrophotometer or a GC/MS system. Plot the concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose a "dump time" which allows ≥85% removal of the corn oil and ≥85% recovery of the bis(2-ethylhexyl)-phthalate. Choose the "collect time" to extend at least 10 minutes after the elution of pentachlorophenol. Wash the column at least 15 minutes between samples. Typical parameters selected are: dump time, 30 minutes (150 mL), collect time, 36 minutes (180 mL) and wash time, 15 minutes (75 mL). The column can also be calibrated by the use of a 254 mm UV detector in place of gravimetric and GC analyses of fractions. Measure the peak areas at various elution times to determine appropriate fractions.

The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. System calibration usually remains constant over this period of time if column flowrate remains constant.

2.2.6.2 GPC Extract Cleanup

Prefilter or load all extracts via the filter holder to avoid particulates that might stop the flow. Load one 5.0 mL aliquot of the extract onto the GPC. Do not apply excessive pressure when loading the GPC. Purge the sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carry-over. Process the extracts using the dump, collect and wash parameters determined from the calibration and collect the cleaned extracts in 400 mL beakers tightly covered with aluminum foil. The phthalate-phenol calibration solution shall be taken through the cleanup cycle with each set of 23 extracts loaded into the GPC. The recovery for each compound must be ≥85%. This must be determined on a GC/FID, using a DB-5 capillary column, a UV recording spectrophotometer or a GC/MS system. A copy of the printouts of standard and check solution are required as deliverables with each case. Show percent recovery on the copy.

2.2.6.3 Concentrate the extract as per paragraphs 2.2.5.7 and 2.2.5.8.

2.2.7 Final Concentration of Extract with Optional Extract Splitting Procedure.

If the extract in paragraph 2.2.5.8 is to be used only for semi-volatile analysis, it must be concentrated to a volume of 1.0 mL, following the procedure in paragraph 2.2.7.2.1.

If the extract in paragraph 2.2.5.8 is to be used for both semi-volatile and pesticide/PCB analyses, then it must be split into two portions. In that case, follow the procedure in paragraph 2.2.7.1 to obtain the pesticide portion, and follow that with the procedure in paragraph 2.2.7.2.2 to obtain the semi-volatile portion.

Refer to Procedure PNL-ALO-347 for specific instructions regarding the treatment of extracts for pesticide analysis.

2.2.7.1 If the same extract is used for both semi-volatile and pesticide/PCB analyses, to split out the pesticide extract, transfer 0.5 mL of the 10 mL methylene chloride extract from paragraph 2.2.5.8 to a separate concentrator tube. Add 5 mL of hexane and a silicon carbide boiling chip and mix using vortex mixer, or if added in this order, allow mixing to occur with boiling. Attach a two-ball micro-Snyder column. Pre-wet Snyder column by adding an apparent volume of 0.5 mL of hexane to the top of the column. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. A longer period of time for the concentration may be required if the temperature is maintained 90°C or less and if the concentration process is performed in a high air flow radiochemistry hood. Concentrate the extract to an apparent volume of between 0.5 and 1 mL. Use Nitrogen blowdown (see paragraph 2.2.7.3) or micro-Snyder column technique (see paragraph 1.5.9) to reduce the volume to 0.5 mL. Add an approximate volume of 0.5 mL of acetone and mix well. The pesticide extract must now be passed through an alumina column to remove the BNA surrogates and polar interferences. Proceed to paragraph 2.2.8 of the pesticide/PCB Procedure PNL-ALO-347.

2.2.7.2 Concentration of the semi-volatile extract.

2.2.7.2.1 If the extract in paragraph 2.2.5.8 was not split to obtain a portion for pesticide analysis, reattach the micro-Snyder column to the concentrator tube used in

paragraph 2.2.5.8 which contains the 10 mL extract and add a fresh silicon carbide boiling chip to the concentrator tube. Pre-wet the Snyder column with an apparent volume of 0.5 mL of methylene chloride. Place the K-D apparatus on the hot water bath (80 - 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. A longer period of time for the concentration may be required if the temperature is maintained 90°C or less and if the concentration process is performed in a high air flow radiochemistry hood. When the apparent volume of the liquid reaches 0.5 mL remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the lower joint into the concentrator tube with an apparent volume of 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with methylene chloride. If GPC cleanup was used, this 1.0 mL represents a two-fold dilution to account for only half of the extract going through the GPC.

2.2.7.2.2 If the extract in paragraph 2.2.5.8 <u>was</u> split in paragraph 2.2.7.1 to obtain a portion for pesticide analysis, reattach the micro-Snyder column to the concentrator tube used in paragraph 2.2.5.8 which contains the 9.5 mL extract and add a fresh silicon carbide boiling chip to the concentrator tube. Pre-wet the Snyder column with an apparent volume of 0.5 mL of methylene chloride. Place the K-D apparatus on the hot water bath (80 - 90°C) so that the concentrator tube inpartially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. A longer period of time for the concentration may be required if the temperature is maintained 90°C or less and if the concentration process is performed in a high air flow radiochemistry hood. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the lower joint into the concentrator tube an apparent volume of 0.2 mL of methylene chloride. Adjust the final volume to 0.95 mL with methylene chloride. If GPC cleanup was used, this 0.95 mL represents a two-fold dilution to account for only

half of the extract going through the GPC, and therefore, the sample detection limit for the sample would be 2x CRQL (see page 4 in Procedure PNL-ALO-345).

2.2.7.3 Nitrogen blowdown technique (taken from ASTM Method D 3086). The following method may be used for final concentration of the BNA extract instead of the procedures in paragraph 2.2.7.2. Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to below 1 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). **CAUTION:** New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

The internal wall of the tube must be rinsed down several times with methylene chloride during the operation. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

If the extract in paragraph 2.2.5.8 was <u>not</u> split for both semi-volatile and pesticide analyses, bring the final volume of the extract to 1.0 mL with methylene chloride. This represents a ten-fold concentration. If the extract in paragraph 2.2.5.8 <u>was</u> split in paragraph 2.2.7.1, then bring the final volume of the semi-volatile portion to 0.95 mL with methylene chloride. This represents a similar ten-fold concentration. In either case, if GPC cleanup techniques were employed, the final volume (1.0 or 0.95 mL) represents a two-fold dilution to account for the fact that only half the extract went through the GPC.

2.2.7.4 Store all extracts at 4°C (±2°C) in the dark in Teflon-sealed containers.

3.0 <u>Records</u>

Records shall be maintained and controlled so as to conform to requirements of the Analytical Chemistry Laboratory Quality Assurance Plan, MCS-033. Bench Sheets and the Organic Analysis Group Standards Laboratory Record Book provide a mechanism for control of records generated in performance of this procedure.

4.0 Specific Qualifications

None required. NIST-traceable surrogate and matrix spike standards are used as part of the QA protocol, and are measured in the self-qualifying procedure PNL-ALO-345.

REFERENCES

USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, 2/88, pages D-7/SV through D-25/SV.

PNL-ALO-120 "Procedure for Extraction of Single Shell Tank Samples for the Analysis of Semivolatile Organic Compounds." Manual PNL-MA-599. Pacific Northwest Laboratory, Richland, WA.

PNL-ALO-225 "Measurement of pH in Aqueous Solutions." Manual PNL-MA-599. Pacific Northwest Laboratory, Richland, WA.

PNL-ALO-340 "Screening of Semivolatiles Organic Extracts," Manual PNL-MA-599. Pacific Northwest Laboratory, Richland, WA.

PNL-ALO-345 "GC/MS Analysis of Extractable Semivolatile Organic Compounds," Manual PNL-MA-599. Pacific Northwest Laboratory, Richland, WA.

PNL-ALO-347 "Sample Preparations for Pesticides/PCBs Analysis in Water and Soil/Sediment," Manual PNL-MA-599. Pacific Northwest Laboratory, Richland, WA.

PNL-ALO-504 "Percent Solids Determination of Solids/Sludges/Solids." Manual PNL-MA-599. Pacific Northwest Laboratory, Richland, WA.

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-345-1
Page 1 of 1

A. Document Number: PNL-ALO-345 Revision Number: 0
Document Title: GC/MS ANALYSIS OF EXTRACTABLE SEMIVOLATILE ORGANIC COMPOUNDS
Document's Original Author: RW Stromatt

Effective Date of ICN: 4/8/91

Change Requested By: RW Stromatt

B. Action:

Replace Applicability Section with that attached.

Pen and ink corrections on original.

C. Effect of Change:

To meet 200-BP-1 requirements

D. Reason for Change/Description of Change

Reason for change - To meet 200-BP-1 client request

Description of change - See attached

E. Approval Signatures

(Please Sign and Date)

Type of Change: (Check (✓) one)

(X) Minor Change ( ) Major Change

~~QSWR~~ Process Quality Department Concurrence: CR Gerber Date: 3/21/91

Approval Authority: [signature] Date: 3/21/91

Other Approvals: WM Dempsie Date: 3/21/91

Date: / /

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-345, GC/MS ANALYSIS OF EXTRACTABLE SEMIVOLATILE ORGANIC COMPOUNDS

APPLICABILITY

This procedure applies to the determination of extractable semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS). After the compounds have been extracted from the sample according to procedure PNL-ALO-120. The compounds covered by this procedure (target compounds) and their contract required quantitation limits (CRQL) are listed in Exhibit C. Concentration and identification are estimated for non-target compounds. The procedure is in the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) 2/88.

Problems can be encountered with target compounds as follows. Dichlorobenzidine and 4-chloroaniline are subject to oxidative losses during solvent extract concentration. Hexachlorocyclopentadiene is subject to thermal decomposition in the GC inlet, chemical reactions in acetone solutions, and photochemical decomposition. N-nitrosodiphenylamine decomposes in the GC inlet forming dephenylamine and thus can not be resolved from diphenylamine present in the sample.

DEFINITIONS

None

RESPONSIBLE STAFF

Cognizant Scientists
Analysts

PROCEDURE

See Attachment 1 for the detailed procedure for this GC/MS analysis of the semivolatile organic compounds.

Author	Date	Project Mgr.	Date	QAD Representative	Date
R W Thomas	7/28/89			S L English	7-28-89
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
C L Lopez	7-28-89	Walter C. Thomas	7/28/89		

Procedure No.	Revision No.	Effective Date	Page	of
PNL-ALO-345	0	AUG 03 1989	1	2

The instrumentation used in this analysis is the Hewlett-Packard HP5890 gas chromatograph and HP5970 mass spectrometer along with Hewlett-Packard printer and terminal peripherals. A Hewlett-Packard HP1000 RTE-A series computer is used as the system controller, data processor, and data report generator.

QUALITY CONTROL

See Attachment 1 for the detailed quality control procedures.

REFERENCES

USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, 2/88, pages D-32/SV through D-45/SV in Exhibit D, E-29/SV through E-46/SV in Exhibit E, and C-4 and C-5 in Exhibit C.

Target Compound List (TCL) and Contract Required Quantitation Limits (CROL)*

Semivolatiles	CAS Number	Quantitation Limits** Water ug/L	Low Soil/Sediment[b] ug/Kg
35. Phenol	108-95-2	10	330
36. bis(2-Chloroethyl) ether	111-44-4	10	330
37. 2-Chlorophenol	95-57-8	10	330
38. 1,3-Dichlorobenzene	541-73-1	10	330
39. 1,4-Dichlorobenzene	106-46-7	10	330
40. Benzyl alcohol	100-51-6	10	330
41. 1,2-Dichlorobenzene	95-50-1	10	330
42. 2-Methylphenol	95-48-7	10	330
43. bis(2-Chloroisopropyl) ether	108-60-1	10	330
44. 4-Methylphenol	106-44-5	10	330
45. N-Nitroso-di-n-dipropylamine	621-64-7	10	330
46. Hexachloroethane	67-72-1	10	330
47. Nitrobenzene	98-95-3	10	330
48. Isophorone	78-59-1	10	330
49. 2-Nitrophenol	88-75-5	10	330
50. 2,4-Dimethylphenol	105-67-9	10	330
51. Benzoic acid	65-85-0	50	1600
52. bis(2-Chloroethoxy) methane	111-91-1	10	330
53 2,4-Dichlorophenol	120-83-2	10	330
54. 1,2,4-Trichlorobenzene	120-82-1	10	330
55. Naphthalene	91-20-3	10	330
56. 4-Chloroaniline	106-47-8	10	330
57. Hexachlorobutadiene	87-68-3	10	330
58. 4-Chloro-3-methylphenol (para-chloro-meta-cresol)	59-50-7	10	330
59. 2-Methylnaphthalene	91-57-6	10	330
60. Hexachlorocyclopentadiene	77-47-4	10	330
61. 2,4,6-Trichlorophenol	88-06-2	10	330
62. 2,4,5-Trichlorophenol	95-95-4	50	1600
63. 2-Chloronaphthalene	91-58-7	10	330
64. 2-Nitroaniline	88-74-4	50	1600
65. Dimethylphthalate	131-11-3	10	330
66. Acenaphthylene	208-96-8	10	330
67. 2,6-Dinitrotoluene	606-20-2	10	330
68. 3-Nitroaniline	99-09-2	50	1600
69. Acenaphthene	83-32-9	10	330

(continued)

Semivolatiles	CAS Number	Quantitation Limits** Water ug/L	Low Soil/Sediment[b] ug/Kg
70. 2,4-Dinitrophenol	51-28-5	50	1600
71. 4-Nitrophenol	100-02-7	50	1600
72. Dibenzofuran	132-64-9	10	330
73. 2,4-Dinitrotoluene	121-14-2	10	330
74. Diethylphthalate	84-66-2	10	330
75. 4-Chlorophenyl-phenyl ether	7005-72-3	10	330
76. Fluorene	86-73-7	10	330
77. 4-Nitroaniline	100-01-6	50	1600
78. 4,6-Dinitro-2-methylphenol	534-52-1	50	1600
79. N-nitrosodiphenylamine	86-30-6	10	330
80. 4-Bromophenyl-phenylether	101-55-3	10	330
81. Hexachlorobenzene	118-74-1	10	330
82. Pentachlorophenol	87-86-5	50	1600
83. Phenanthrene	85-01-8	10	330
84. Anthracene	120-12-7	10	330
85. Di-n-butylphthalate	84-74-2	10	330
86. Fluoranthene	206-44-0	10	330
87. Pyrene	129-00-0	10	330
88. Butylbenzylphthalate	85-68-7	10	330
89. 3,3'-Dichlorobenzidine	91-94-1	20	660
90. Benzo(a)anthracene	56-55-3	10	330
91. Chrysene	218-01-9	10	330
92. bis(2-Ethylhexyl)phthalate	117-81-7	10	330
93. Di-n-octylphthalate	117-84-0	10	330
94. Benzo(b)fluoranthene	205-99-2	10	330
95. Benzo(k)fluoranthene	207-08-9	10	330
96. Benzo(a)pyrene	50-32-8	10	330
97. Indeno(1,2,3-cd)pyrene	193-39-5	10	330
98. Dibenz(a,h)anthracene	53-70-3	10	330
99. Benzo(g,h,i)perylene	191-24-2	10	330

[b] Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for SemiVolatile TCL Compounds are 60 times the individual Low Soil/Sediment CRQL.

* Specific quantitation limits are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

** Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher.

1. Summary of Method

This method is to be used for the GC/MS analysis of semivolatiles screened by Section III protocols and for confirmation of pesticides/PCBs identified by GC/EC, if concentrations permit.

2. Apparatus and Materials

2.1 Gas chromatograph/mass spectrometer system.

2.1.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns and gases.

2.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm) bonded-phase silicone coated fused silica capillary column (J&W Scientific DB-5 or equivalent). A film thickness of 1.0 micron is recommended because of its larger capacity. A film thickness of 0.25 micron may be used.

2.1.3 Mass Spectrometer - Capable of scanning from 35 to 500 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all required criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet. NOTE: DFTPP criteria must be met before any sample extracts are analyzed. Any samples analyzed when DFTPP criteria have not been met will require reanalysis at no cost to the Government.

2.1.4 Data system - A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

3. Reagents

3.1 Internal standards - 1,4 dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}.

An internal standard solution can be prepared by dissolving 200 mg of each compound in 50 mL of methylene chloride. It may be necessary to use 5 to 10 percent benzene or toluene in this solution and a few minutes of ultrasonic mixing in order to dissolve all the constituents. The resulting solution will contain each standard at a concentration of 4000 ng/uL. A 10 uL portion of this solution should be added to each 1

mL of sample extract. This will give a concentration of 40 ng/uL of each constituent.

3.2 Prepare calibration standards at a minimum of five concentration levels. Each calibration standard should contain each compound of interest and each surrogate standard. (See GC/MS calibration in Exhibit E for calibration standard concentration.)Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10°C to -20°C in screw-cap amber bottles with teflon liners. Fresh standards should be prepared every twelve months at a minimum. The continuing calibration standard should be prepared weekly and stored at 4°C (±2°C).

4. Calibration

4.1 Each GC/MS system must have the hardware tuned to meet the criteria listed in Exhibit E for a 50 ng injection of decafluorotriphenyl phosphine (DFTPP). No sample analyses can begin until all these criteria are met. This criteria must be demonstrated each 12 hour shift. DFTPP has to be injected to meet this criterion. Post-acquisition manipulation of abundances is not acceptable.

4.2 The internal standards selected in paragraph 2.3.1 should permit most components of interest in a chromatogram to have retention times of 0.80 to 1.20 relative to the internal standards (see instructions for Form VI, Initial Calibration Data). Use the base peak ion from the specific internal standard as the primary ion for quantification, found in Exhibit E, Table 2.2. If interferences are noted, use the next most intense ion as the secondary ion, i.e. For 1,4-dichlorobenzene-d_4 use m/z 152 for quantification.

4.2.1 The internal standards are added to all calibration standards and all sample extracts just prior to analysis by GC/MS. A 10 uL aliquot of the internal standard solution should be added to a 1 mL aliquot of calibration standards.

4.3 Analyze 1 uL of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. Calculate relative response factors (RRF) for each compound using Equation 1.

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

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 standard from Exhibit E.

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

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

4.3.1 The average relative response factor (RRF) should be calculated for all compounds. A system performance check must be made before this calibration curve is used. Four compounds (the system performance check compounds) are checked for a minimum average relative response factor. These compounds (the SPCC) are N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, 4-nitrophenol. See instructions in Exhibit E for Form VI, Initial Calibration Data for more details.

4.3.2 A % Relative Standard Deviation (%RSD) is calculated for thirteen compounds labeled the Calibration Check Compounds (CCC) on Form VI SV and in Table 2.3, Exhibit E, III SV. A maximum % RSD is also specified for these compounds. These criteria must be met for the calibration curve to be valid.

4.4 A check of the calibration curve must be performed once every 12 hours during analysis. These criteria are described in detail in the instructions for Form VII, Calibration Check. The minimum relative response factor for the system performance check compounds must be checked. If this criteria is met, the relative response factors of all compounds are calculated. A percent difference of the daily (12 hour) relative response factor compared to the average relative response factor from the initial curve is calculated. A maximum percent difference is allowed for each compound flagged as 'CCC' on Form VII. Only after both these criteria are met can sample analysis begin.

4.5 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each standard. If EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

5. <u>GC/MS Analysis</u>

5.1 The following instrumental parameters are required for all performance tests and for all sample analyses:

Electron Energy - 70 volts (nominal)
Mass Range - 35 to 500 amu
Scan Time - not to exceed 1 second per scan

5.2 Combine 0.5 mL of the base/neutral extract and 0.5 mL of acid from the water extract prior to analysis.

5.3 Internal standard solution is added to each sample extract. For water and/or medium soil extracts, add 10 uL of internal standard solution to each accurately measured 1.0 mL of sample extract. If the low soil

extracts required a pesticide split (see Section II, Part C, paragraph 2.7), add 9.5 uL of internal standard solution to each accurately measured 0.95 mL of sample extract. Analyze the 1.0 mL extract by GC/MS using a bonded-phase silicone-coated fused silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial Column Temperature Hold	–	40°C for 4 minutes
Column Temperature Program	–	40-270°C at 10 degrees/min.
Final Column Temperature Hold	–	270°C for 10 minutes
Injector Temperature	–	250-300°C
Transfer Line Temperature	–	250-300°C
Source Temperature	–	according to manufacturer's specifications
Injector	–	Grob-type, splitless
Sample Volume	–	1 - 2 uL
Carrier Gas	–	Helium at 30 cm^3/sec

NOTE: Make any extract dilution indicated by characterization prior to the addition of internal standards. If any further dilutions of water or soil/sediment extracts are made, additional internal standards must be added to maintain the required 40 ng/uL of each constituent in the extract volume. If the concentration on the column of any compound exceeds the initial calibration range, the extract must be diluted and reanalyzed. See Exhibit E, Section III, SV, Part 6. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the Case Narrative.

6. Qualitative Analysis

6.1 The compounds listed in the Target Compound List (TCL), Exhibit C, shall be identified by an analyst competent in the interpretation of mass spectra (see PreAward Bid Confirmation description) by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

6.1.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate

assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

6.1.2 For comparison of standard and sample component mass spectra, mass spectra obtained on the contractor's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the contractor's GC/MS meets the DFTPP daily tuning requirements. These standard spectra may be obtained from the run used to obtain reference RRTs.

6.1.3 The requirements for qualitative verification by comparison of mass spectra are as follows:

6.1.3.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

6.1.3.2 The relative intensities of ions specified in (1) must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)

6.1.3.3 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. In Task III, the verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the CRQL report the actual value followed by "J", e.g. "3J."

6.1.4 If a compound cannot be verified by all of the criteria in 6.1.3, but in the technical judgement of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantification in 7.

6.2 A library search shall be executed for non-TCL sample components for the purpose of tentative identification. For this purpose, the 1985 release of the National Bureau of Standards Mass Spectral Library (or more recent release), containing 42,261 spectra, shall be used.

6.2.1 Up to 20 nonsurrogate organic compounds of greatest apparent concentration not listed in Exhibit C for the combined base/neutral/acid fraction shall be tentatively identified via a forward search of the NBS mass spectral library. (Substances with responses less than 10% of the nearest internal standard are not required to be searched in this fashion). Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist

assign a tentative identification. NOTE: Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

6.2.2 Guidelines for making tentative identification:

6.2.2.1 Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

6.2.2.2 The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)

6.2.2.3 Molecular ions present in reference spectrum should be present in sample spectrum.

6.2.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

6.2.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting compounds. NOTE: Data system library reduction programs can sometimes create these discrepancies.

6.2.3 If in the technical judgement of the mass interpretation spectral specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

7. Quantitation

7.1 TCL components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte (see Exhibit E, Tables 2.1 and 2.2). The EICP area of characteristic ions of analytes listed in Tables 4, 5 and 6 are used.

Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and

corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike and matrix spike duplicate. The criteria are described in detail in the instructions for Form VIII, Internal Standard Area Summary. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. If the analysis of a subsequent sample or standard indicates that the system is functioning properly, then corrections may not be required. The samples or standards with EICP areas outside the limits must be re-analyzed, and treated according to 7.1.1 and 7.1.2 below. If corrections are made, then the laboratory must demonstrate that the mass spectrometric system is functioning properly. This must be accomplished by the analysis of a standard or sample that <u>does</u> meet the EICP criteria. After corrections are made, the re-analysis of samples analyzed while the system was malfunctioning is required.

7.1.1 If after re-analysis, the EICP areas for all internal standards are inside the contract limits (-50% to +100%), then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, <u>only submit</u> data from the analysis with EICPs within the contract limits. This is considered the <u>initial</u> analysis and must be reported as such on all data deliverables.

7.1.2 If the re-analysis of the sample does not solve the problem, i.e., the EICP areas are outside the contract limits for both analyses, then submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the re-analysis on all data deliverables, using the sample suffixes specified in Exhibit B. Document in the Case Narrative all inspection and corrective actions taken.

7.2 The relative response factor (RRF) from the daily standard analysis is used to calculate the concentration in the sample. Secondary ions may be used if interferences are present. The area of a secondary ion cannot be substituted for the area of a primary ion unless a relative response factor is calculated using the secondary ion. When TCL Compounds are below contract required quantitation limits (CRQL) but the spectra meets the identification criteria, report the concentration with a "J." For example, if CRQL is 10 ug/L and concentration of 3 ug/L is calculated, report as "3J."

7.2.1 Calculate the concentration in the sample using the relative response factor (RRF) as determined in paragraph 4.3 and the following equation:

Water

$$\text{Concentration ug/L} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RRF)(V_o)(V_i)}$$

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

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard injected in nanograms (ng)

V_o = Volume of water extracted in milliliters (mL)

V_i = Volume of extract injected (uL)

V_t = Volume of total extract

(Use 2000 uL or a factor of this when dilutions are made. The 2,000 uL is derived from combining half of the 1 mL BN extract and half of the 1 mL A extract.)

Soil/Sediment

$$\text{Concentration (Dry weight basis) ug/kg} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RRF)(V_i)(W_s)(D)}$$

Where:

A_x, I_s, A_{is} = Same as given for water, above

V_t = Volume of low level total extract (Use 1000 uL or a factor of this when dilutions are made. If GPC cleanup is used, the volume is 2,000 uL. The 1000 uL is derived from concentrating the 9.5 mL extract to 0.95 mL.)

- OR -

V_t = Volume of medium level extract (Use 2,000 uL or a factor of this when dilutions are made. The 2,000 uL is derived from concentrating 5 mL of the 10 mL extract to 1 mL.)

V_i = Volume of extract injected (uL)

D = $\frac{100 - \%\ \text{moisture}}{100}$

W_s = Weight of sample extracted (grams)

7.3 An estimated concentration for non-TCL components tentatively identified shall be quantified by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used.

7.3.1 The formula for calculating concentrations is the same as in paragraph 7.2.1. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

7.4 Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if recovery is within limits and report on appropriate form.

7.4.1 If recovery is not within limits (i.e., if two surrogates from either base/neutral or acid fractions are out of limits or if recovery of any one surrogate in either fraction is below 10%), the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Reanalyze the sample if none of the above reveal a problem.

7.4.2 If the reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the contract windows. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

7.4.3 If none of the steps in 7.4.1 or 7.4.2 solve the problem, then reextract and reanalyze the sample. If the reextraction and reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the contract windows. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

7.4.4 If the reextraction and reanalysis of the sample does not solve the problem, i.e., the surrogate recoveries are outside the contract limits for both analyses, then submit the surrogate spike recovery data and the sample analysis data from analysis of both sample extracts. Distinguish between the initial analysis and the reanalysis on all data deliverables, using the sample suffixes specified in Exhibit B.

7.4.5 If the sample with surrogate recoveries outside the limits is the sample used for the matrix spike and matrix spike duplicate and the surrogate recoveries of the matrix spike and matrix spike duplicate show the same pattern (i.e., outside the limits), then the sample, matrix spike and matrix spike duplicate do not require re-analysis.

Document in the narrative the similarity in surrogate recoveries.

Table 4.

Characteristic Ions for Semivolatile TCL Compounds

Parameter	Primary Ion	Secondary Ion(s)
Phenol	94	65, 66
bis(-2-Chloroethyl)Ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
Benzyl Alcohol	108	79, 77
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	108	107
bis(2-chloroisopropyl)Ether	45	77, 79
4-Methylphenol	108	107
N-Nitroso-Di-Propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
Benzoic Acid	122	105, 77
bis(-2-Chloroethoxy)Methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-Methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127

(continued)

Table 4. (continued)
Characteristic Ions for Semivolatile TCL Compounds

Parameter	Primary Ion	Secondary Ion(s)
2-Nitroaniline	65	92, 138
Dimethyl Phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-Methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Di-N-Butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)Anthracene	228	229, 226
bis(2-Ethylhexyl)Phthalate	149	167, 279
Chrysene	228	226, 229
Di-N-Octyl Phthalate	149	-
Benzo(b)Fluoranthene	252	253, 125
Benzo(k)Fluoranthene	252	253, 125
Benzo(a)Pyrene	252	253, 125
Indeno(1,2,3-cd)Pyrene	276	138, 227
Dibenz(a, h)Anthracene	278	139, 279
Benzo(g, h, i)Perylene	276	138, 277

Table 5.

Characteristic Ions for Pesticides/PCBs

Parameter	Primary Ion	Secondary Ion(s)
Alpha-BHC	183	181, 109
Beta-BHC	181	183, 109
Delta-BHC	183	181, 109
Gamma-BHC (Lindane)	183	181, 109
Heptachlor	100	272, 274
Aldrin	66	263, 220
Heptachlor Epoxide	353	355, 351
Endosulfan I	195	339, 341
Dieldrin	79	263, 279
4,4'-DDE	246	248, 176
Endrin	263	82, 81
Endosulfan II	337	339, 341
4,4'-DDD	235	237, 165
Endosulfan Sulfate	272	387, 422
4,4'-DDT	235	237, 165
Methoxychlor	227	228
Chlordane (alpha and/or gamma)	373	375, 377
Toxaphene	159	231, 233
Aroclor-1016	222	260, 292
Aroclor-1221	190	222, 260
Aroclor-1232	190	222, 260
Aroclor-1242	222	256, 292
Aroclor-1248	292	362, 326
Aroclor-1254	292	362, 326
Aroclor-1260	360	362, 394
Endrin Ketone	317	67, 319

Table 6.

Characteristic Ions for Surrogates and
Internal Standards for Semivolatile Compounds

SURROGATES	Primary Ion	Secondary Ion(s)
Phenol-d_5	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
d-5 Nitrobenzene	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212
INTERNAL STANDARDS		
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenapthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265

This Section outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with the determination of semivolatile organic TCL compounds in water and soil/sediment samples. These QC operations are as follows:

- o Documentation of GC/MS Mass Calibration and Abundance Pattern
- o Documentation of GC/MS Response Factor Stability
- o Internal Standard Response and Retention Time Monitoring
- o Method Blank Analysis
- o Surrogate Spike Response Monitoring
- o Matrix Spike and Matrix Spike Duplicate Analysis

PART 1 - TUNING AND GC/MS MASS CALIBRATION

1. Summary

It is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria prior to initiating any on-going data collection. This is accomplished through the analysis of Decafluorotriphenylphosphine (DFTPP).

Definition: The twelve (12) hour time period for GC/MS system tuning and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of a compliant tune. The time period ends after twelve (12) hours has elapsed according to the system clock.

1.1 Decafluorotriphenylphosphine (DFTPP)

1.1.1 Each GC/MS system used for the analysis of semivolatile or pesticide TCL compounds must be hardware tuned to meet the abundance criteria listed in Table 1.2 for a 50 ng injection of decafluorotriphenylphosphine (DFTPP). DFTPP may be analyzed separately or as part of the calibration standard. The criteria must be demonstrated daily or for each twelve (12) hour period, whichever is more frequent, before samples can be analyzed. DFTPP must be injected to meet this criterion. If required, background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the contract specifications are unacceptable. NOTE: All instrument conditions must be identical to those used in sample analysis, except that a different temperature program may be used.

1.1.2 Whenever the Contractor takes corrective action which may change or affect the tuning criteria for DFTPP (e.g., ion source cleaning or repair, etc.), the tune must be verified irrespective of the 12-hour tuning requirements.

TABLE 1.2. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30.0 - 60.0 percent of mass 198
68	less than 2.0 percent of mass 69
70	less than 2.0 percent of mass 69
127	40.0 - 60.0 percent of mass 198
197	less than 1.0 percent of mass 198
198	base peak, 100 percent relative abundance
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	greater than 1.00 percent of mass 198
441	present but less than mass 443
442	greater than 40.0 percent of mass 198
443	17.0 - 23.0 percent of mass 442

1.2 Documentation

The Contractor shall provide documentation of the calibration in the form of a bar graph spectrum and as a mass listing.

1.2.1 The Contractor shall complete a Form V (GC/MS Tuning and Mass Calibration) each time an analytical system is tuned. In addition, all samples, standards, blanks, matrix spikes, and matrix spike duplicates analyzed during a particular tune must be summarized in chronological order on the bottom of the appropriate Form V. Detailed instructions for the completion of Form V are found in Exhibit B, Section III.

PART 2 - CALIBRATION OF THE GC/MS SYSTEM

2. Summary

Prior to the analysis of samples and required 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.

2.1 Prepare calibration standards as described in Exhibit D SV, Section IV, to yield the following specific concentrations:

2.1.1 Semivolatile TCL Compounds

Initial calibration of semivolatile TCL compounds is required at 20, 50, 80, 120, and 160 total nanograms. If an analyte saturates at the 160 total nanogram concentration level, and the GC/MS system is calibrated to achieve a detection sensitivity of no less than the CRQL, the laboratory must document it on Form VI and in the Case Narrative, and attach a quantitation report and RIC. In this instance, the laboratory

should calculate the results based on a four-point initial calibration for the specific analyte. The use of a secondary ion for quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the Case Narrative. Nine compounds: Benzoic Acid, 2,4-Dinitrophenol, 2,4,5-Trichlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, 4,6-Dinitro-2-Methylphenol, and Pentachlorophenol will only require a four-point initial calibration at 50, 80, 120, and 160 total nanograms since detection at less than 50 nanograms per injection is difficult.

2.2 The USEPA plans to develop performance based criteria for response factor data acquired during this program. To accomplish this goal, the Agency has specified both the concentration levels for initial calibration and has also specified the specific internal standard to be used on a compound-by-compound basis for quantitation (Table 2.2). Establishment of standard calibration procedures is necessary and deviations by the Contractor will not be allowed.

2.3 Analyze each calibration standard and tabulate the area of the primary characteristic ion (Exhibit D SV, Table 4) against concentration for each compound including all contract required surrogate compounds. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late eluting compounds usually will have much better agreement.

Using Table 2.2, calculate the relative response factors (RRF) for each compound at each concentration level using Equation 2.1.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x} \qquad \text{Eq. 2.1}$$

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 2.1 or 2.2.
C_{is} = Concentration of the internal standard (ng/uL).
C_x = Concentration of the compound to be measured (ng/uL).

2.3.1 Using the relative response factors (RRF) from the initial calibration, calculate the percent relative standard deviations (%RSD) for compounds labeled on Form VI as Calibration Check Compounds and shown in Table 2.3 (see 2.6.2) using Equation 2.2.

$$\%RSD = \frac{SD}{\bar{x}} \times 100 \qquad \text{Eq. 2.2}$$

where,

RSD = Relative Standard Deviation

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

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

$\bar{x}$ = 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.

2.4 A system performance check must be performed to ensure that minimum average relative response factors are met before the calibration curve is used.

2.4.1 For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-Nitroso-Di-n-Propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol and 4-Nitrophenol. The minimum acceptable average relative response factor (RRF) for these compounds is 0.050. SPCCs typically have very low RRFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. These compounds are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

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

2.5 Documentation

Once the initial calibration is validated, calculate and report the average relative response factor (RRF) and percent relative standard deviation (%RSD) for all TCL compounds. The Contractor shall complete and submit Form V (the GC/MS tune for the initial calibration) and Form VI (Initial Calibration Data) for each instrument used to analyze samples under this protocol. Detailed instructions for completion of Form VI are in Exhibit B, Section III.

2.6 Continuing Calibration

A calibration standard(s) containing all semivolatile TCL compounds, including all required surrogates, must be analyzed each twelve hours during analysis (see definition of twelve hour time period, paragraph 1. of this Section). Compare the relative response factor data from the standards each twelve hours with the average relative response factor from the initial calibration for a specific instrument. A system performance check must be made each twelve hours. If the SPCC

TABLE 2.2. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING TCL ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}	Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
Phenol	Nitrobenzene	Hexachlorocyclo-pentadiene	4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octyl Phthalate
bis(2-Chloroethyl) ether	Isophorone	2,4,6-Trichloro-phenol	N-nitrosodi-phenylamine	Butylbenzyl Phthalate	Benzo(b)fluor-anthene
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichloro-phenol	1,2-Diphenylhy-drazine	3,3'-Dichloro-benzidine	Benzo(k)fluor-anthene
1,3-Dichlorobenzene	2,4-Dimethyl-phenol	2-Chloronaphthalene	4-Bromophenyl Phenyl Ether	Benzo(a)-anthracene	Benzo(a)pyrene
1,4-Dichlorobenzene	Benzoic acid	2-Nitroaniline	Hexachloro-benzene	bis(2-ethylhexyl) Phthalate	Indeno(1,2,3-cd) pyrene
Benzyl Alcohol	bis(2-Chloro-ethoxy)methane	Dimethyl Phthalate	Pentachloro-phenol	Chrysene	Dibenz(a,h) anthracene
1,2-Dichlorobenzene	2,4-Dichloro-phenol	Acenaphthylene	Phenanthrene	Terphenyl-d_{14} (surr)	Benzo(g,h,i) perylene
2-Methylphenol	1,2,4-Trichloro-benzene	3-Nitroaniline	Anthracene		
bis(2-Chloroiso-propyl)ether	Naphthalene	Acenaphthene	Di-n-butyl Phthalate		
4-Methylphenol	4-Chloroaniline	2,4-Dinitrophenol	Fluoranthene		
N-nitroso-Di-n-propylamine	Hexachloro-butadiene	4-Nitrophenol			
Hexachloroethane	4-Chloro-3-methylphenol	Dibenzofuran			
2-Fluorophenol (surr)	2-Methylnaphth-alene	2,4-Dinitrotoluene			
Phenol-d_6 (surr)	Nitrobenzene-d_5 (surr)	2,6-Dinitrotoluene			
		Diethyl Phthalate			
		4-Chlorophenyl phenyl ether			
		Fluorene			
		4-Nitroaniline			
		2-Fluorobiphenyl (surr)			
		2,4,6-Tribromo Phenol (surr)			

Surr = surrogate compound

criteria are met, a comparison of relative response factors is made for all compounds. This is the same check that is applied during the initial calibration (Form VI). If the minimum relative response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins.

2.6.1 Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatography system. This check must be met before analysis begins. The minimum relative response factor (RRF) for semivolatile System Performance Check Compounds (SPCC) is 0.050.

2.6.2 Calibration Check Compounds (CCC)

After the system performance check is met, Calibration Check Compounds listed in Table 2.3 are used to check the validity of the initial calibration. Calculate the percent difference using Equation 2.3.

$$\% \text{ Difference} = \frac{\overline{RRF_I} - RRF_c}{\overline{RRF_I}} \times 100 \qquad \text{Eq. 2.3}$$

where,

$\overline{RRF_I}$ = average response factor from initial calibration.

RRF_c = response factor from current verification check standard.

2.6.2.1 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 has been taken, a new initial five point calibration MUST be generated. These criteria MUST be met before sample analysis begins.

TABLE 2.3. CALIBRATION CHECK COMPOUNDS

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

2.6.3 Concentration Levels for Continuing Calibration Check

The USEPA plans to evaluate the long term stability of response factors during this program. Standardization among contract laboratories is necessary to reach these long term goals. Along with contract specified concentrations for initial calibration, the USEPA is requiring specific concentrations for each continuing calibration standard(s).

2.6.3.1 The concentration for each semivolatile TCL compound in the continuing calibration standard(s) is 50 total nanograms for all compounds.

2.7 Documentation

The Contractor shall complete and submit a Form VII for each GC/MS system utilized for each twelve hour time period. Calculate and report the relative response factor and percent difference (%D) for all compounds. Ensure that the minimum RRF for semivolatile SPCCs is 0.050. The percent difference (%D) for each CCC compound must be less than or equal to 25.0 percent. Additional instructions for completing Form VII are found in Exhibit B, Section III.

PART 3 - METHOD BLANK ANALYSIS

3. Summary

A method blank is a volume of deionized, distilled laboratory water for water samples, or a purified solid matrix for soil/sediment samples, carried through the entire analytical scheme (extraction, concentration, and analysis). For soil/sediment samples, a solid matrix suitable for semivolatile analyses is available from EMSL/LV. The method blank volume or weight must be approximately equal to the sample volumes or sample weights being processed.

3.1 Method blank analysis must be performed at the following frequency.

3.1.1 For the analysis of semivolatile TCL compounds, a method blank analysis must be performed once:

- each Case, OR
- each 14 calendar day period during which samples in a Case are received (said period beginning with the receipt of the first sample in that Sample Delivery Group), OR
- each 20 samples in a Case, including matrix spikes and reanalyses, that are of similar matrix (water or soil) or similar concentration (soil only), OR
- whenever samples are extracted by the same procedure (separatory funnel, continuous liquid-liquid extraction, or sonication),

whichever is most frequent, on each GC/MS or GC system used to analyze samples.

3.2 It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

3.2.1 For the purposes of this protocol, an acceptable laboratory method blank should meet the criteria of paragraphs 3.2.1.1 and 3.2.1.2.

3.2.1.1 A method blank for semivolatile analysis must contain less than or equal to five times (5X) the Contract Required Quantitation Limit (CRQL from Exhibit C) of the phthalate esters in the TCL.

3.2.1.2 For all other TCL compounds not listed above, the method blank must contain less than or equal to the Contract Required Quantitation Limit of any single TCL analyte.

3.2.2 If a laboratory method blank exceeds these criteria, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) MUST be reextracted and reanalyzed at no additional cost to the Agency. The Laboratory Manager, or his designee, must address problems and solutions in the Case Narrative (Exhibit B).

3.3 Documentation

The Contractor shall report results of method blank analysis using the Organic Analysis Data Sheet (Form I) and the form for tentatively identified compounds (Form I, TIC). In addition, the samples associated with each method blank must be summarized on Form IV (Method

Blank Summary). Detailed instructions for the completion of these forms are in Exhibit B, Section III.

3.3.1 The Contractor shall report ALL sample concentration data as UNCORRECTED for blanks.

PART 4 - SURROGATE SPIKE (SS) ANALYSIS

4. Summary

Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before purging or extraction in order to monitor preparation and analysis of samples.

4.1 Each sample, matrix spike, matrix spike duplicate, and blank are spiked with surrogate compounds prior to extraction. The surrogate spiking compounds shown in Table 4.1 are used to fortify each sample, matrix spike, matrix spike duplicate, and blank with the proper concentrations. Performance based criteria are generated from laboratory results. Therefore, deviations from the spiking protocol will not be permitted.

TABLE 4.1. SURROGATE SPIKING COMPOUNDS

Compounds	Amount in Sample Extract* (before any optional dilutions)		
	Fraction	Water	Low/Medium Soil
Nitrobenzene-d_5	BNA	50 ug	50 ug
2-Fluorobiphenyl	BNA	50 ug	50 ug
p-Terphenyl-d_{14}	BNA	50 ug	50 ug
Phenol-d_5	BNA	100 ug	100 ug
2-Fluorophenol	BNA	100 ug	100 ug
2,4,6-Tribromophenol	BNA	100 ug	100 ug

* At the time of injection.

4.2 Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the contract required recovery limits listed in Table 4.2.

TABLE 4.2. CONTRACT REQUIRED SURROGATE SPIKE RECOVERY LIMITS

Fraction	Surrogate Compound	Water	Low/Medium Soil
BNA	Nitrobenzene-d_5	35-114	23-120
BNA	2-Fluorobiphenyl	43-116	30-115
BNA	p-Terphenyl-d_{14}	33-141	18-137
BNA	Phenol-d_5	10-94	24-113
BNA	2-Fluorophenol	21-100	25-121
BNA	2,4,6-Tribromophenol	10-123	19-122

4.3 Treatment of surrogate spike recovery information is according to paragraphs 4.3.1 through 4.3.2.

4.3.1 Method Blank Surrogate Spike Recovery

The laboratory must take the actions listed below if recovery of any one surrogate compound in either the base/neutral or acid fraction is outside of contract surrogate spike recovery limits.

4.3.1.1 Check calculations to ensure that there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc; also check instrument performance.

4.3.1.2 Reanalyze the blank extract if steps in 4.3.1.1 fail to reveal the cause of the noncompliant surrogate recoveries.

4.3.1.3 Reextract and reanalyze the blank.

4.3.1.4 If the measures listed in 4.3.1.1 thru 4.3.1.3 fail to correct the problem, the analytical system must be considered to be out of control. The problem MUST be corrected before continuing. This may mean recalibrating the instrumentation but it may also mean more extensive action. The specific corrective action is left up to the GC/MS operator. When surrogate recovery(ies) in the blank is outside of the contract required windows, all samples associated with that blank MUST be reanalyzed at no additional cost to the Agency.

4.3.2 Sample Surrogate Spike Recovery

The laboratory must take the actions listed below if either of the following conditions exists:

- Recovery of any one surrogate compound in either base neutral or acid fraction is below 10%.

- Recoveries of two surrogate compounds in either base neutral or acid fractions are outside surrogate spike recovery limits.

4.3.2.1 The Contractor shall document (in this instance, document means to write down and discuss the problem and corrective action taken in the Case Narrative, see Exhibit B) deviations outside of acceptable quality control limits and take the following actions:

4.3.2.1.1 Check calculations to ensure that there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc.; also check instrument performance.

4.3.2.1.2 If the steps in 4.3.2.1.1 fail to reveal a problem, then reanalyze the extract. If reanalysis of the extract solves the problem, then the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the contract windows. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

4.3.2.1.3 If the steps in 4.3.2.1.2 fail to solve the problem, then reextract and reanalyze the sample. If the reextraction and reanalysis solves the problem, then the problem was in the laboratory's control. Therefore, only submit data from the extraction and analysis with surrogate spike recoveries within the contract windows. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

If the reextraction and reanalysis of the sample does not solve the problem; i.e., surrogate recoveries are outside the contract windows for both analyses, then submit the surrogate spike recovery data and the sample data from both analyses according to paragraph 4.4. Distinguish between the initial analysis and the reanalysis on all data

deliverables, using the sample suffixes specified in Exhibit B.

4.4 Documentation

The Contractor shall report surrogate recovery data for the following:

- Method Blank Analysis
- Sample Analysis
- Matrix Spike/Matrix Spike Duplicate Analyses
- All sample reanalyses that substantiate a matrix effect

The surrogate spike recovery data is summarized on the Surrogate Spike Percent Recovery Summary (Form II). Detailed instructions for the completion of Form II are in Exhibit B, Section III.

PART 5 - MATRIX SPIKE/MATRIX SPIKE DUPLICATE ANALYSIS (MS/MSD)

5. Summary

In order to evaluate the matrix effect of the sample upon the analytical methodology, the USEPA has developed the standard mixes listed in Table 5.1 to be used for matrix spike and matrix spike duplicate analyses. These compounds are subject to change depending upon availability and suitability for use as matrix spikes.

5.1 MS/MSD Frequency of Analysis

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 field samples of a similar concentration level (soils only), OR
- each 14 calendar day period during which field 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.

5.2 Use the compounds listed in Table 5.1 to prepare matrix spiking solutions according to protocols described in Exhibit D SV. The analytical protocols in Exhibit D SV stipulate the amount of matrix spiking solution to be added to the sample aliquots prior to extraction. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate samples.

TABLE 5.1. MATRIX SPIKING SOLUTIONS

Base/Neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-Methylphenol
N-Nitroso-Di-n-Propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

5.2.1 Samples requiring optional dilutions and chosen as the matrix spike/ matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

5.3 Individual component recoveries of the matrix spike are calculated using Equation 5.1.

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100 \qquad \text{Eq. 5.1}$$

where

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

5.4 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 5.2.

$$RPD = \frac{D1 - D2}{(D1 + D2)/2} \times 100 \qquad \text{Eq. 5.2}$$

where

RPD = Relative Percent Difference
D1 = First Sample Value
D2 = Second Sample Value (duplicate)

5.5 Documentation

The matrix spike (MS) results (concentrations) for nonspiked semivolatile TCL compounds shall be reported on Form I (Organic Analysis Data Sheet) and the matrix spike percent recoveries shall be summarized on Form III (MS/MSD Recovery). These values will be used by

EPA to periodically update existing performance based QC recovery limits (Table 5.2).

The results for nonspiked semivolatile TCL compounds in the matrix spike duplicate (MSD) analysis shall be reported on Form I (Organic Analysis Data Sheet) and the percent recovery and the relative percent difference shall be summarized on Form III (MS/MSD Recovery). The RPD data will be used by EPA to evaluate the long term precision of the analytical method. Detailed instructions for the completion of Form III are in Exhibit B, Section III.

TABLE 5.2. MATRIX SPIKE RECOVERY LIMITS*

Fraction	Matrix Spike Compound	Water	Soil/Sediment
BN	1,2,4-Trichlorobenzene	39-98	38-107
BN	Acenaphthene	46-118	31-137
BN	2,4-Dinitrotoluene	24-96	28-89
BN	Pyrene	26-127	35-142
BN	N-Nitroso-Di-n-Propylamine	41-116	41-126
BN	1,4-Dichlorobenzene	36-97	28-104
Acid	Pentachlorophenol	9-103	17-109
Acid	Phenol	12-89	26-90
Acid	2-Chlorophenol	27-123	25-102
Acid	4-Chloro-3-Methylphenol	23-97	26-103
Acid	4-Nitrophenol	10-80	11-114

PART 6 - SAMPLE ANALYSIS

6. Summary

The intent of Part 6 is to provide the Contractor with a brief summary of ongoing QC activities involved with sample analysis. Specific references are provided to help the Contractor meet specific reporting and deliverables requirements of this contract.

6.1 Sample Analysis

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 (described in Part 2 of this Section). Any major system maintenance, such as a source cleaning or installation of a new column, may necessitate a retune and recalibration (see Initial Calibration, Part 2). Minor maintenance should necessitate only the calibration verification (Continuing Calibration, Part 2).

6.1.1 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. The criteria are described in detail in the instructions for Form VIII, Internal Standard Area Summary (see Exhibit B, Section III). 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 or cleaning the injector sleeve 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.

6.1.1.1 If after reanalysis, the EICP areas for all internal standards are inside the contract 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 EICPs within the contract limits. This is considered the initial analysis and must be reported as such on all data deliverables.

6.1.1.2 If the reanalysis of the sample does not solve the problem, i.e., the EICP areas are outside contract 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, using the sample suffixes specified in Exhibit B. Document in the Case Narrative all inspection and corrective actions taken.

6.1.2 Each analytical run must also be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound. The initial method calibration (Part 2) requires that the system should not be saturated for high response compounds at 160 nanograms for semivolatile TCL compounds.

6.1.2.1 If the on-column concentration of any compound in any sample exceeds the initial calibration range, that sample must be diluted, the internal standard concentration readjusted, and the sample reinjected, as described in specific methodologies in Exhibit D SV. Secondary ion quantitation is only allowed when

there are sample matrix interferences with the primary ion.

6.1.2.2 If the dilution of the sample causes any compound detected in the first analysis to be undetectable in the second analysis, then the results of both analyses shall be reported on separate Forms I, according to the instructions in Exhibit B.

6.1.3 Qualitative Analysis

The semivolatile compounds listed in the Target Compound List (TCL), Exhibit C, shall be identified by an analyst competent in the interpretation of mass spectra, by comparison of the suspect mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra (see Exhibit D SV, Section IV).

6.1.3.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample.

6.1.3.2 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/MS are required. The DFTPP tuning requirements listed in Part 1 must be met on the same GC/MS.

6.1.3.2.1 The requirements for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
- The relative intensities of ions specified in the above paragraph must agree within ±20% between the standard and sample spectra.
- Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. When GC/MS computer data processing programs are used to obtain the sample

component spectrum, both the processed and the raw spectra must be evaluated. In Task III, the verification process should favor false negatives (Exhibit D SV, Section IV).

6.1.3.2.2 If a compound cannot be verified by all of the criteria in 6.1.3.2.1, but in the technical judgement of the mass spectral interpretation specialist the identification is correct, the Contractor shall report the identification and proceed with the quantitation.

6.1.3.3 A library search shall be executed for nonsurrogate and non-TCL sample components for the purpose of tentative identification. For this purpose, the 1985 or most recent available version of the National Bureau of Standards Mass Spectral Library, containing 42,261 spectra, should be used.

6.1.4 Quantitation

6.1.4.1 Semivolatile TCL components identified shall be quantitated by the internal standard method. The internal standards used shall be the ones assigned in Table 2.2 of this Section. The EICP area of characteristic ions of TCL analytes are used (Exhibit D SV, Section IV).

6.1.4.2 An estimated concentration for non-TCL components tentatively identified shall be quantitated by the internal standard method. For quantification, the nearest internal standard free of interferences must be used.

6.1.4.3 Calculate surrogate standard recovery (see Part 4) for all surrogate compounds on all samples, blanks, matrix spikes, and matrix spike duplicates. If recovery is within contractual limits, report on Form II (see Exhibit B, Section III). If recovery is outside contractual limits, take specific steps listed in Surrogate Spike Recoveries (Part 4).

6.1.4.4 Calculate matrix spike and matrix spike duplicate percent recovery (see Part 5) for all compounds and report results on Form III (see Exhibit B, Section III). Calculate Relative Percent Differences (RPDs) for all matrix spiking compounds and report results on Form III. Ensure that the proper frequency of MS/MSD analysis is maintained.

6.1.5 **Reporting and Deliverables**

Refer to Exhibit B of this Statement of Work for specific details on contract deliverables and reporting formats. Exhibit B contains specific instructions for completing all required Forms, as well as a detailed itemization of reporting and deliverables requirements. Exhibit H contains the format requirements for delivery of data in computer-readable format.

APPLICABILITY

This procedure applies to the determination of extractable semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS) after the samples have been screened to estimate organic concentrations according to the procedure PNL-ALO-340 and extracted from the sample according to procedure PNL-ALO-344. The compounds covered by this procedure (target compounds) and their contract required quantitation limits (CRQL) are listed in Exhibit C. Concentration and identification are estimated for non-target compounds. The procedure is in the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) 2/88.

Problems can be encountered with target compounds as follows. Dischlorobenzidine and 4-chloroaniline are subject to oxidative losses during solvent extract concentration. Hexachlorocyclopentadiene is subject to thermal decomposition in the CG inlet, chemical reactions in acetone solutions, and photochemical decomposition. N-nitrosodiphenylamine decomposes in the GC inlet forming dephenylamine and thus can not be resolved from diphenylamine present in the sample.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-346, ANALYSIS FOR PESTICIDES/PCBs BY GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

APPLICABILITY

This procedure applies to the determination of pesticide and PCB compounds by gas chromatography with electron capture detection (GC/ECD) after sample preparation described in PNL-ALO-34_. The compounds covered in this procedure and their quantitation limits are listed in attachment 1, page C-6.

DEFINITIONS

None

RESPONSIBLE STAFF

- Cognizant scientist
- Analyst

PROCEDURE

See Attachment 1 for the detailed procedure for this GC/ECD analysis of pesticide and PCB compounds. This procedure is the pesticides/PCB procedure in the USEPA CLP SOW 2/88 for Organics Analysis.

QUALITY CONTROL

See Attachment 1 for the detailed quality control procedures.

REFERENCES

USEPA Contract Laboratory Program Statement Of Work For Organic Analysis, Multi-Media, Multi-Concentration, 2/88, pages D-34/PEST through D-49/PEST in exhibit D, E-48/PEST through E-64/PEST in exhibit E. Page D-34a, Revision 9/88, provides for use of wide-bore capillary columns.

Author	Date	Project Mgr.	Date	QAD Representative	Date
	1-30-91	B.M. Gallegos	1-30-91	GK Geeke	1/31/91
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
	1-30-91		1/30/91		

Procedure No.	Revision No.	Effective Date	Page	of
PNL-ALO-346	0	APR 26 1991	1	1

Target Compound List (TCL) and Contract Required Quantitation Limits (CROL)*

Pesticides/PCBs	CAS Number	Quantitation Limits** Water ug/L	Low Soil/Sediment[c] ug/Kg
100. alpha-BHC	319-84-6	0.05	8.0
101. beta-BHC	319-85-7	0.05	8.0
102. delta-BHC	319-86-8	0.05	8.0
103. gamma-BHC (Lindane)	58-89-9	0.05	8.0
104. Heptachlor	76-44-8	0.05	8.0
105. Aldrin	309-00-2	0.05	8.0
106. Heptachlor epoxide	1024-57-3	0.05	8.0
107. Endosulfan I	959-98-8	0.05	8.0
108. Dieldrin	60-57-1	0.10	16.0
109. 4,4'-DDE	72-55-9	0.10	16.0
110. Endrin	72-20-8	0.10	16.0
111. Endosulfan II	33213-65-9	0.10	16.0
112. 4,4'-DDD	72-54-8	0.10	16.0
113. Endosulfan sulfate	1031-07-8	0.10	16.0
114. 4,4'-DDT	50-29-3	0.10	16.0
115. Methoxychlor	72-43-5	0.5	80.0
116. Endrin ketone	53494-70-5	0.10	16.0
117. alpha-Chlordane	5103-71-9	0.5	80.0
118. gamma-Chlordane	5103-74-2	0.5	80.0
119. Toxaphene	8001-35-2	1.0	160.0
120. Aroclor-1016	12674-11-2	0.5	80.0
121. Aroclor-1221	11104-28-2	0.5	80.0
122. Aroclor-1232	11141-16-5	0.5	80.0
123. Aroclor-1242	53469-21-9	0.5	80.0
124. Aroclor-1248	12672-29-6	0.5	80.0
125. Aroclor-1254	11097-69-1	1.0	160.0
126. Aroclor-1260	11096-82-5	1.0	160.0

[c] Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Pesticide/PCB TCL compounds are 15 times the individual Low Soil/Sediment CRQL.

* Specific quantitation limits are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

** Quantitation limits listed for soil/sediment are based on wet weight. The quantitation Limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher.

1. Summary of Method

1.1 The hexane extracts of water and soil/sediment are analyzed on a gas chromatograph/electron capture detector (GC/EC). If pesticides or PCBs are tentatively identified, a second GC/EC analysis is required using an alternate column. Quantitation must be on a packed column, whereas, confirmation can be on either a packed or a capillary column. NOTE: To determine that no pesticides/PCBs are present at or above the contract required quantitation limit is a form of quantitation.

2. Interferences

2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

3. Apparatus and Materials

3.1 Gas chromatograph - An analytical system complete with gas chromatograph and all required accessories including syringes, analytical columns, gases, electron capture detector and strip-chart recorder with recording integrator. A data system is required for measuring peak areas or peak heights and recording retention times. An electrolytic conductivity detector is also acceptable if the required quantitation limits are met. Overlapping peaks on chromatograms are not acceptable.

3.1.1 Quantitation and/or confirmation columns.

3.1.1.1 Column 1 - Gas Chrom Q (100/120 mesh) or equivalent coated with 1.5% OV-17/1.95% OV-210 or equivalent packed in a 1.8m long x 4 mm ID (6 mm OD) glass column.

NOTE: The 2mm ID column cited in Table 7 as Column 1 will not adequately separate dibutylchlorendate and endrin ketone.

3.1.1.2 Column 2 - Gas Chrom Q (100/120 mesh) or equivalent coated with 3% OV-1 or equivalent packed in a 1.8 m long x 2 mm ID (6 mm OD) glass column.

3.1.1.3 Column 3 - Gas Chrom Q (80/100 mesh) or equivalent coated with 5% OV-210 or equivalent packed in a 1.8 m long x 2 mm ID (6 mm OD) glass column.

3.1.2 Confirmation column only. Column - 30 m X 0.25 mm ID, 0.25 micron film thickness, bonded-phase silicone coated, fused silica capillary column (J&W Scientific DB-5 or DB-1701 or equivalent). NOTE: DB-1701 provides better separation of TCL

Column 1 above. However, wide bore columns such as DB-5 or DB-1701 may provide equivalent performance. It is the responsibility of the Contractor to demonstrate the equivalence of any wide bore columns employed for these analyses. Equivalence is demonstrated by meeting all of the performance criteria for pesticide analyses given in Exhibit D and E. Such data should be kept on file by the laboratory, and be available during on-site evaluations.

3.1.2 Confirmation column only. Column - 30 m X 0.25 mm ID, 0.25 micron film thickness, bonded-phase silicone coated, fused silica capillary column (J&W Scientific DB-5 or DB-1701 or equivalent). NOTE: DB-1701 provides better separation of TCL

pesticides. Column 10 m x 0.32 mm ID, 1 micron film thickness has been used.

3.2 Balance - analytical, capable of accurately weighing ±0.0001 g.

4. Reagents

4.1 Isooctane (2,2,4-trimethylpentane), hexane and toluene - Pesticide quality or equivalent.

4.2 Stock standard solutions (1.00 ug/uL) - Stock standard solution can be prepared from pure standard materials or purchased as certified solutions.

4.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in toluene, dilute to volume in a 10 mL volumetric flask with isooctane. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are traceable to EMSL/LV supplied standards.

4.2.2 Transfer the stock standard solutions into a bottle/vial with Teflon-lined septa. Store at 4°C (±2°C) and protect from light. Stock standard solutions must be replaced after twelve months, or sooner if comparison with check standards indicate a problem.

4.3 Working standards solutions - Prepare mixtures of standards diluted with hexane that will provide approximately half scale response for all the compounds of interest. This should be at the attenuation setting capable of achieving the contract-required quantitation limits (Exhibit C). (This would be approximately 0.01 ng/uL for aldrin.) Two mixtures of the individual component standards are recommended to prevent co-elution of components on packed columns. However, all individual component standards may be included in one mixture on packed or capillary columns if the laboratory demonstrates that the components may be separated with no overlap of peaks. Include dibutylchlorendate in all standard mixtures. All multicomponent standards, i.e., PCB Aroclors and toxaphene must be in separate solutions with the exception of Aroclors 1016/1260. Include dibutylchlorendate in all multicomponent standard mixtures.

4.3.1 Evaluation Standard Mixtures - Prepare working standard mixtures diluted with hexane containing aldrin, endrin, 4,4' DDT and dibutylchlorendate to evaluate the GC column. Prepare three concentration levels to provide the following criteria:

4.3.1.1 Low level will be approximately 20% above base line (Evaluation Standard Mix A).

4.3.1.2 Mid level will be approximately half scale (Evaluation Standard Mix B).

4.3.1.3 High level will be approximately full scale (Evaluation Standard Mix C). (Dibutylchlorendate must be 0.1 ng/uL to correspond with 100% surrogate recovery in 10 mL final volume. This may be slightly greater than full scale but should still be in linear range).

4.3.2 Individual Standard Mixtures - These include all single component TCL pesticides plus alpha chlordane, gamma chlordane, endrin ketone, endrin aldehyde and dibutylchlorendate (see paragraph 6.1.4 for suggested mixtures). Alpha and gamma chlordane should be in Mixture B to avoid overlap with other pesticides.

5. Calibration

5.1 The gas chromatographic system must be calibrated using the external standard technique for all packed columns used for quantitation.

5.2 External standard calibration procedure:

5.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane. One of the external standards should be at a concentration near, but above, the CRQL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. This should be done on each quantitation column and each instrument at the beginning of the contract period and each time a new column is installed. The data must be retained by the laboratory and made available for inspection during on-site evaluations.

5.2.2 Using injections of 2 to 5 uL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound.

6. GC/EC Primary Analysis (Quantitation may be performed on primary or confirmation analyses.)

Adjust oven temperature and carrier gas flow rates so that the retention time for 4,4'-DDT is equal to or greater than 12 minutes.

Table 7 provides examples of operating conditions for the gas chromatograph. Separation should be $\geq$ 25% resolution between peaks. Percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criterion must be considered when determining whether to quantitate on the Primary Analysis or the Confirmation Analysis. When

this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

6.1 Inject 2 to 5 uL of the sample or standard extract using the solvent-flush technique or auto sampler. Smaller (1.0 uL) volumes can be injected only if automatic devices are employed. Record the volume injected to the nearest 0.05 uL and the total extract volume. NOTE: Dibutylchlorendate recovery may be calculated from a capillary or packed column GC/EC meeting all QC requirements for quantitation. However, matrix spike duplicates must be quantitated on a packed column.

6.1.1 Inject Individual Standard Mix A and B and all multiresponse pesticides/PCBs at the beginning of each 72 hour sequence. (See paragraph 6.1.3.5) To establish the RT window within each 72-hour sequence for the pesticide/PCB of interest, use the absolute RT from the above chromatograms as the mid-point, and ± three times the standard deviation calculated in Exhibit E for each compound. Individual Standard Mix A and B are analyzed alternately and intermittently throughout the analysis as shown in 6.1.3.5. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The laboratory must reanalyze all affected samples.

6.1.2 Sample analysis of extracts from Section II, Sample Preparation, can begin when linearity and degradation QA/QC requirements specified in Exhibit E have been met.

NOTE: The 10.0% RSD linearity criterion is only required on the column(s) being used for pesticide/PCBs quantitation. If a column is used for surrogate quantitation only, the 10.0% RSD is required only for dibutylchlorendate.

Analyze samples in groups of no more than 5 samples. After the analysis of the first group of up to 5 samples, analyze Evaluation Mix B. Analyze another group of up to 5 samples, followed by the analysis of Individual Mix A or B. Subsequent groups of up to 5 samples may be analyzed by repeating this sequence, alternately analyzing Evaluation Mix B and Individual Mix A or B between the groups as shown in 6.1.3.5. The Pesticide/PCB analytical sequence must end with Individual Mix A and B regardless of the number of samples analyzed (see 6.1.3.5).

If a multiresponse pesticide/PCB is detected in either of the preceding groups of 5 samples, the appropriate multiresponse pesticide/PCB may be substituted for Individual Mix A or B. All standards listed in 6.1.3.5 must be included for every Case and must be analyzed within the same 72-hour period as the samples, with the exception of Aroclors 1221 and 1232 which are analyzed at a minimum of once per month (see footnote in 6.1.3.5). If the samples are split between 2 or more instruments, the

complete set of standards must be analyzed on each instrument with the same 72-hour requirement. All standards must be analyzed prior to the samples to avoid the effects of poor chromatography caused by the unsuspected injection of a highly concentrated sample.

6.1.3 Paragraphs 6.1.3.1 - 6.1.3.5 contain GC performance criteria. If it is determined during the course of a 72-hour sequence that one or more of the criteria have been violated, stop the run and take corrective action (see Exhibit E, Section III PEST, 4.3.3.8). After the corrective action has been taken, the 72-hour sequence may be restarted as follows. If a standard violated the criterion, restart the sequence with that standard, determine that the criteria have been met and continue with sample analyses, according to 6.1.3.5. If a sample violated the criterion, restart the sequence with the standard that would have <u>followed</u> that group of samples (thereby preserving the sequence of standards in 6.1.3.5), determine that the criteria have been met and continue with sample analyses, according to 6.1.3.5.

If it is determined after the completion of a 72-hour sequence that one or more of the criteria have been violated, proceed as follows. If a standard violated the criterion, all samples analyzed after that standard must be re-analyzed as part of a new 72-hour sequence. If a subsequent standard in the original sequence met all the criteria, then only those samples analyzed between the standard that did not meet the criterion and the standard that did meet the criterion must be re-analyzed as part of a new 72-hour sequence. If only samples violated the criteria, then those samples must be re-analyzed as part of a new 72-hour sequence.

6.1.3.1 Differences in the Calibration Factors for each standard in Individual Standard Mix A and B must not exceed 20.0% (15.0% for any standard compound used for quantitation) during the 72-hour Primary Analysis. Calculate the % difference using the initial Individual Standard Mix versus all subsequent Individual Standard Mixes analyzed during the 72-nour sequence. (The equations for calculation of Calibration Factor and % difference are in Exhibit E, Section III PEST, paragraph 4:3.4.2.) NOTE: To determine that no pesticides/PCBs are present at or above the contract required quantitation limit <u>is</u> a form of quantitation.

The retention time shift of dibutylchlorendate in any standard or sample must be less than 2.0% difference for packed columns, less than 1.5% difference for wide bore capillary columns (ID greater than 0.32 mm) and less than 0.3% difference

for narrow bore capillary columns (ID less than 0.32 mm).

6.1.3.2 Samples must also be repeated if the degradation of DDT and/or endrin exceeds 20.0% respectively on the intermittent analysis of Evaluation Standard Mix B.

6.1.3.3 All pesticide standards must fall within the established 72-hour retention time windows.

6.1.3.4 Highly colored extracts may require a dilution.

6.1.3.5 The 72-hour sequence must be as follows.

72-Hour Sequence for Pesticide/PCB Analysis:

1. Evaluation Standard Mix A
2. Evaluation Standard Mix B
3. Evaluation Standard Mix C
4. Individual Standard Mix A*
5. Individual Standard Mix B*
6. Toxaphene
7. Aroclors 1016/1260
8. Aroclor 1221**
9. Aroclor 1232**
10. Aroclor 1242
11. Aroclor 1248
12. Aroclor 1254
13. 5 samples
14. Evaluation Standard Mix B
15. 5 samples
16. Individual Standard Mix A or B
17. 5 samples
18. Evaluation Standard Mix B
19. 5 samples
20. Individual Standard Mix A or B (whichever not run in step 16)
21. 5 samples
22. Repeat the above sequence starting with Evaluation Standard Mix B (step 14 above).
23. Pesticide/PCB analysis sequence must end with the analyses of <u>both</u> Individual Standard Mix A <u>and</u> B regardless of number of samples analyzed.

*These may be combined into one mixture (see paragraph 4.3).

**Aroclors 1221 and 1232 must be analyzed on each instrument and each column at a minimum of <u>once per month</u>.

Copies of these chromatograms must be submitted for sample analyses performed during the applicable month.

6.1.4 Suggested groups of compounds and concentrations for Individual Standard Mix A and B follow, which are recommended to prevent overlap of compounds on the two packed columns (3% OV-1 and 1.5% OV-17/1.95% OV-210). Some of the compounds overlap on the 5% OV-210 column (see Table 7). The concentration is based on a 5 uL injection.

Individual Standard Mix A	ng/uL	Individual Standard Mix B	ng/uL
gamma-BHC	0.005	alpha-BHC	0.005
heptachlor	0.010	beta-BHC	0.010
aldrin*	0.010	delta-BHC	0.010
heptachlor epoxide	0.010	aldrin*	0.010
endosulfan I	0.010	p,p'-DDE	0.010
dieldrin	0.010	endrin	0.010
p,p'-DDT	0.020	p,p'-DDD	0.020
endrin aldehyde	0.025	endosulfan sulfate	0.020
endosulfan II	0.020	endrin ketone	0.020
methoxychlor	0.100	alpha chlordane	0.010
dibutylchlorendate	0.050	gamma chlordane	0.010
		dibutylchlorendate	0.050

*For RRT determination.

6.1.5 Inject the method blank (extracted with each set of samples) on every instrument and GC column on which the samples are analyzed.

6.2 Evaluation of Chromatograms.

6.2.1 Consider the sample negative when its peaks, depending on the pesticide's response factor, result in concentrations less than the required quantitation level. The sample is complete at this point. Confirmation is not required.

6.2.2 Tentative identification is made when the unknown's retention time matches the retention time of a corresponding standard that was chromatographed on the same instrument within a 72-hour period.

6.2.3 Determine if any pesticides/PCBs listed in Exhibit C are present. Pattern recognition techniques, based on chromatograms of standards, are recommended for the identification of PCB compounds.

6.2.3.1 If the response for any of these compounds is 100% or less of full scale, the extract is ready for confirmation and quantitation.

6.2.3.2 If the response for any compound is greater than full scale, dilute the extract so that the peak will be between 50 and 100% full scale and reanalyze on the packed column. Use this dilution also for confirmation and quantitation.

6.2.3.3 For dilution >10 fold. Also inject an aliquot of a dilution 10 fold more concentrated to determine if other compounds of interest are present at lower concentrations.

6.2.3.4 Computer reproductions of chromatograms manipulated to ensure all peaks are on scale over a 100 fold range are an accepted substitute. However, this can be no greater than a 100 fold range. This is to prevent retention time shifts by column or detector overload. Linearity must be demonstrated over the 100 fold range using higher concentrations of the evaluation mixture.

6.2.4 Quantitation may be performed on the primary analysis, with the exception of toxaphene and possibly the DDT series. If DDT exceeds the 10.0% RSD linearity criterion, then quantitations for any DDE, DDD and DDT in a sample must be on the confirmation analysis. Toxaphene must always be quantitated on the confirmation analysis. See Exhibit E for special QC requirements for quantitation.

6.2.5 If identification of compounds of interest are prevented by the presence of interferences, further cleanup is required. If sulfur is evident go to Sulfur Cleanup (Section II, Part B, paragraph 8.). If unknown interferences or poor chromatography are noted only in the sample chromatogram, it is recommended that gel permeation chromatography cleanup (Section II, Part C, paragraph 2.6) be applied.

6.2.6 When selecting a GC column for confirmation and/or quantitation, be sure that none of the compounds to be confirmed/quantitated overlap, i.e., do not select the 3% OV-1 column if DDE and dieldrin are to be confirmed and/or quantitated. When samples are very complex, it may be necessary to use all three packed columns to achieve adequate separation (≥25% resolution) of all compounds being quantitated.

7. <u>GC/EC Confirmation Analysis</u>

7.1 Confirmation Analysis is to confirm the presence of all compounds tentatively identified in the Primary Analysis. Therefore, the only standards that are required are the Evaluation Standard Mixes (to check linearity and degradation criteria) and standards of all compounds to be confirmed. The linearity criterion on the confirmation column for pesticides is not required unless the column is used for quantitation. The 72-hour sequence in 6.1.3.5 is, therefore, modified

to fit each case. Quantitation may be performed on the confirmation analysis. If toxaphene or DDT is to be quantitated, additional linearity requirements are specified in 7.3.1.

7.2 Table 7 provides examples of operating conditions for the gas chromatograph. Separation should be ≥25% resolution between peaks. Percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criterion must be considered when determining whether to quantitate on the Primary Analysis or the Confirmation Analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

For a fused silica capillary column (FSCC) confirmation, there must be ≥25 percent resolution (valley) between the following pesticide pairs:

- beta-BHC and delta-BHC
- Dieldrin and 4,4'-DDT
- 4,4'-DDD and Endrin Aldehyde
- Endosulfan Sulfate and 4,4'-DDT

All QC requirements specified in Exhibit E must be adhered to, i.e., the ≥12 min. retention time for 4,4'-DDT, the criteria for 4,4'-DDT and endrin degradation, linearity, calibration factor for standards and retention time shift for dibutylchlorendate. The retention time criterion for 4,4'-DDT does <u>not</u> have to be met if the confirmation column is OV-1 or OV-101. Apply instructions from 6.1.3 to the confirmation analysis.

7.3 Inject 2 to 5 uL (1-2 uL for capillary columns) of the sample extract and standards using the solvent-flush technique or auto samplers. A volume of 1 uL can be injected only if automatic devices are employed. Record the volume injected to the nearest 0.05 uL and the total extract volume. The detector attenuation must provide peak response equivalent to the Primary Analysis response for each compound to be confirmed.

7.3.1 Begin the Confirmation Analysis GC sequence with the three concentration levels of Evaluation Standard Mixes A, B and C. The exception to this occurs when toxaphene and/or DDT series are to be confirmed and quantitated. There are four combinations of pesticides that could occur, therefore, the following sequences must be followed depending on the situation.

7.3.1.1 Toxaphene only - Begin the sequence with Evaluation Mix B to check degradation, followed by three concentration levels of toxaphene. Check linearity by calculating %RSD.

If ≤10.0% RSD, use the appropriate equation in paragraph 8 for calculation. If >10.0% RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

7.3.1.2 DDT, DDE, DDD only - Begin the sequence with Evaluation Mix B. Then inject three concentration levels of a standard containing DDE, DDD and DDT. Calculate linearity and follow the requirements specified in 7.3.1.1 for each compound to be quantitated.

7.3.1.3 DDT series and toxaphene - Begin the sequence with Evaluation Mix B. Then inject three concentration levels of toxaphene and another three levels of the DDT series. Calculate linearity and follow the requirements specified in 7.3.1.1 for each compound to be quantitated. NOTE: Capillary quantitation would be allowed only in this situation.

7.3.1.4 Other pesticides/PCBs plus DDT series and/or toxaphene – Begin the sequence with Evaluation Standard Mixes A, B and C. Calculate linearity on the four compounds in the Evaluation Standard mixes. If DDT and/or one or more of the other compounds are >10.0% RSD and/or degradation exceeds the criterion, corrective maintenance as outlined in Exhibit E, Section III PEST, paragraph 4.3.3.8, should be performed before repeating the above chromatography evaluations. If only DDT exceeds the linearity criterion and one or more of the DDT series is to be quantitated, follow 7.3.1.2 (do not repeat Evaluation Mix B).

If none of the DDT series is to be quantitated and DDT exceeds the 10.0% RSD, simply record the % RSD on the proper form. Any time toxaphene is to be quantitated, follow 7.3.1.1.

7.3.2 After the linearity standards required in 7.3.1 are injected, continue the confirmation analysis sequence by injecting standards for all compounds tentatively identified in the primary analysis, to establish the 72-hour retention time windows. (See paragraph 6.1.1.) Analyze all confirmation standards for a case at the beginning, at intervals specified in 7.3.3 and at the end. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The laboratory must reanalyze all samples which follow the standard that exceeds the criterion.

7.3.3 After injection of the appropriate standards (see 7.3.2), begin injection of samples. Analyze groups of 5 samples. Analyze Evaluation Mix B after the first group of 5 samples. After the second group of 5 samples, analyze a standard pertaining to the samples in the preceding groups (i.e., substitute standards pertaining to the preceding samples for Individual Mix A or B in 6.1.3.5). Continue analyzing groups of 5 samples, alternately analyzing Evaluation Mix B and standards pertaining

to the preceding samples between groups of 5 samples. The alternating standard's calibration factors must be within 15.0% of each other if quantitation is performed. Deviations larger than 15.0% require the laboratory to repeat the analyses of samples which were analyzed after the standard that exceeded the criterion. The 15.0% criterion only pertains to compounds being quantitated.

If more than one standard is required to confirm all compounds tentatively identified in the Primary Analysis, alternate the standards with Evaluation Mix B. Samples must also be repeated if the degradation of either DDT and/or endrin exceeds 20.0% on the intermittent Evaluation Standard Mix B.

If the samples are split between 2 or more instruments, all standards and blanks pertaining to those samples must be analyzed on each instrument.

7.3.4 Inject the method blank (extracted with each set of samples) on every GC and GC column on which the samples are analyzed.

7.4 Evaluation of Chromatograms

7.4.1 A compound tentatively identified in the primary analysis is confirmed if the retention time from the confirmation analysis falls within the retention time window of a corresponding standard that was chromatographed on the same instrument within a 72-hour period.

7.4.2 Quantitation should be on the packed column chromatogram (primary or confirmation) that provides the best separation from interfering peaks. NOTE: To determine that no pesticides/PCBS are present at or above the contract required quantitation limit is a form of quantitation.

7.4.2.1 Quantitation of Chlordane - Because weathering and/or different formulations of chlordane usually modify the pattern exhibited by technical chlordane, this method is not appropriate for determining technical chlordane. Instead, standards for alpha chlordane and gamma chlordane are used for quantitation, and each isomer of chlordane is reported separately.

7.4.3 Computer reproductions of chromatograms that are attenuated to ensure all peaks are on scale over a 100 fold range are acceptable. However, this can be no greater than a 100 fold range. This is to prevent retention time shifts by column or detector overload. Also, peak response must be >25% of full scale deflection to allow visual pattern recognition of multicomponent compounds, and individual compounds must be visible.

7.4.4 If identification of compounds of interest are prevented by the presence of interferences, further cleanup is required. If sulfur is evident, go to Sulfur Cleanup (Section II, Part B, paragraph 8).

If unknown interferences or poor chromatography are noted only in the sample chromatogram, it is recommended that gel permeation chromatography cleanup (Section II, Part C, paragraph 2.6) be applied.

7.4.5 Calculate surrogate standard recovery on all samples, blanks and spikes unless the surrogate was diluted out. Determine if recovery is within limits and report on Form II. See formula for calculation in 8.3.

7.4.6 If TCL pesticide/PCB compounds were identified in the unspiked sample from which the matrix spike and matrix spike duplicate were prepared, confirmation analysis is required for the matrix spike and matrix spike duplicate. If TCL pesticide/PCB compounds were not identified in the unspiked sample, confirmation of the matrix spike and matrix spike duplicate is not required. Calculate matrix spike duplicate recoveries and report on Form III (see Exhibit B, Section III).

8. Calculations

8.1 Calculate the concentration in the sample using the following equation for external standards. Response can be measured by the manual peak height technique or by automated peak height or peak area measurements from an integrator.

8.1.1 Water

$$\text{Concentration ug/L} = \frac{(A_x)(I_s)(V_t)}{(A_s)(V_i)(V_s)}$$

Where:

A_x = Response for the parameter to be measured.
A_s = Response for the external standard.
V_t = Volume of total extract (uL) (take into account any dilutions)
I_s = Amount of standard injected in nanograms (ng)
V_i = Volume of extract injected (uL)
V_s = Volume of water extracted (mL)

8.1.2 Sediment/Soil

$$\text{Concentration (Dry weight basis) ug/kg} = \frac{(A_x)(I_s)(V_t)}{(A_s)(V_i)(W_s)(D)}$$

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Where:

A_x, I_s, A_s, V_i = same as given above in 8.1.1

V_t = Volume of <u>low level</u> total extract (Use 20,000 uL or a factor of this when dilutions are made other than those accounted for below):
- 1/20 total extract taken for pesticide analysis (derived from 0.5 mL of 10 mL extract)
- final concentration to 1.0 mL for pesticide analysis

- or -

V_t = Volume of <u>medium level</u> total extract (Use 10,000 uL or a factor of this when dilutions are made.)

$D = \frac{100 - \%\ \text{moisture}}{100}$ (% moisture from Section II, Part C)

W_s = Weight of sample extracted (g)

8.2 For multicomponent mixtures (chlordane, toxaphene and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak (>50% of the total area must be used) unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

8.3 Calculation for surrogate and matrix spike recoveries.

$$\text{Percent Recovery} = \frac{Q_d}{Q_a} \times 100\%$$

where,

Q_d = quantity determined by analysis

Q_a = quantity added to sample.

Be sure all dilutions are taken into account. Soil/Sediment has a 20-fold dilution factor built into the method when accounting for one-twentieth of extract taken for pesticide analysis and final dilution to 1 mL.

8.4 Report results in micrograms per liter or micrograms per kilogram <u>without correction</u> for recovery data.

9. GC/MS Confirmation of Pesticides

9.1 Any compounds confirmed by two columns must also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS. The following paragraphs should be used as guidance when determining if a pesticide/PCB compound can be confirmed by GC/MS.

9.1.1 The GC/MS analysis normally requires a minimum concentration of 10 ng/uL in the final extract, for each single component compound. For the BNA extract of a water sample, a concentration of 10 ng/uL in extract is approximately 20 ug/L (ppb) in the sample. For the BNA extract of a low level soil sample, the equivalent sample concentration would be approximatly 170 ug/Kg if no GPC was performed. For the BNA extract of a medium soil, the equivalent sample concentration is on the order of 10,000 ug/Kg.

9.1.2 The pesticide extract and associated blank should be analyzed by GC/MS as per Exhibit D SV, Section IV, paragraph 5.

9.1.3 The confirmation may be from the GC/MS analysis of the semivolatile extracts (sample and blank). However, if the compounds are not detected in the semivolatile extract even though the concentration is high enough, a GC/MS analysis of the pesticide extract is required.

9.1.4 A reference standard for the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the pesticides/PCBs identified by GC/EC. Use the sample concentration calculated from the GC/EC results as guidance. The concentration of the reference standards must be no greater than the sample extract concentration predicted from the GC/EC sample concentration. For instance, as in paragraph 9.1.1 above, a 20 ug/L sample result from GC/EC requires a 10 ng/uL GC/MS reference standards in order to demonstrate adequate sensitivity for a water sample.

9.1.5 In the event the GC/MS does not confirm the presence of the pesticides/PCBs identified by GC/ECD, those compounds should be reported as not detected. The minimum quantitation limits ("U" values) should be adjusted to reflect the interferences. The inability to confirm the compounds by GC/MS must be noted in the Case Narrative.

9.1.6 For GC/MS confirmation of multicomponent pesticides and PCBs, required deliverables are spectra of 3 major peaks of multicomponent compounds from samples and standards.

9.1.7 Quantitation by GC/MS must use the characteristic quantitation ions for pesticides/PCBs given in Table 5 of Exhibit D SV.

Table 7

Examples of Orders of Elution of Pesticides/PCBs

Parameter	Column 1	Column 2	Column 3
alpha-BHC	1.45	1.64	1.86
gamma-BHC	1.86	1.94	2.37
beta-BHC	2.18	1.76	2.75
Heptachlor	2.27	3.21	2.55
delta-BHC	2.55	2.01	2.80
Aldrin	2.76	4.01	2.93
Heptachlor epoxide	4.31	4.98	5.53
Endosulfan I	5.46	6.26	7.08
4,4'-DDE	6.37	7.51	6.03
Dieldrin	6.74	7.38	8.59
Endrin	8.25	8.35	10.14
4,4'-DDD	10.08	9.53	10.57
Endosulfan II	10.14	8.35	12.88
4,4'-DDT	12.06	12.75	11.55
Endrin aldehyde	13.64	9.53	21.11
Endosulfan sulfate	16.73	11.09	31.27
Endrin ketone	22.70	-	33.16
gamma Chlordane	4.77	5.74	5.25
alpha Chlordane	5.24	6.39	5.70
Toxaphene	mr	mr	mr
Aroclor-1016	mr	mr	mr
Aroclor-1221	mr	mr	mr
Aroclor-1232	mr	mr	mr
Aroclor-1242	mr	mr	mr
Aroclor-1248	mr	mr	mr
Aroclor-1254	mr	mr	mr
Aroclor-1260	mr	mr	mr
methoxychlor	24.07	19.60	18.12
dibutylchlorendate	21.80	27.21	22.26

mr = multiresponse compounds.

Column 1 conditions: Gas Chrom Q (80/100 mesh) or equivalent coated with 1.5% OV-17/1.95% OV-210 or equivalent packed in a 1.8 m long x 2 mm ID (6 mm OD) glass column with 5% methane/95% argon carrier gas at a flow rate of 30 mL/min. (HP 5880) Column temperature, isothermal at 192°C. 2 mm ID column with 80/100 mesh does not adequately resolve dibutyl chlorendate and endrin ketone.

Column 2 conditions: Gas Chrom Q (100/120 mesh) or equivalent coated with 3% OV-1 or equivalent packed in a 1.8 m long x 2 mm ID (6 mm OD) glass column with 5% methane/95% argon carrier gas at a flow rate of 30 mL/min. (30 mL/min makeup gas). (Tracor 222). Column temperature, isothermal at 194°C.

Table 7 (continued)

Column 3 conditions: Gas Chrom Q (80/100 mesh) or equivalent coated with 5% OV-210 packed in a 1.8 m x 2 mm ID (6 mm OD) glass column with 5% methane/ 95% argon carrier gas at a flow rate of 30 mL/min. (30 mL/min. make-up gas). HP5840. Column temperature, isothermal at 183°C.

Capillary column 1 conditions: 30 m x 0.25 mm ID, 0.25 micron film thickness, fused silica DB-5 (or equivalent) splitless mode

Helium carrier gas: 4 mL/min at 280°C and 25 PSI
Septum purge: 15 mL/min
Split vent: none
Initial temperature: 160°C, initial hold - 2 min
Program at 5°C/min
Final temperature: 270°C, final hold - 4 min
Injection port temperature: 225°C

Capillary column 2 conditions: 10 m x 0.32 mm ID, 1 micron film thickness, fused silica DB-1701, splitless mode

Helium carrier gas: 4 mL/min at 280°C and 25 PSI
Septum purge: 15 mL/min
Split vent: none
Initial temperature: 160°C, initial hold - 3 min
Program at 10°C/min to 240°C
Program from 240 to 270°C at 5°C/min
Final Hold: 4 min
Injection port temperature: 235°C

This Section outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with the determination of pesticide/PCB organic TCL compounds in water and soil/sediment samples. These QC operations are as follows:

- Method Blank Analysis
- Surrogate Spike Response Monitoring
- Matrix Spike and Matrix Spike Duplicate Analysis
- Specific QA/QC for Pesticide Analysis

PART 1 - METHOD BLANK ANALYSIS

1. Summary

A method blank is a volume of deionized, distilled laboratory water for water samples, or a purified solid matrix for soil/sediment samples, carried through the entire analytical scheme (extraction, concentration, and analysis). For soil/sediment samples, a solid matrix suitable for pesticide analyses is available from EMSL-LV. The method blank volume or weight must be approximately equal to the sample volumes or sample weights being processed.

1.1 Method blank analysis must be performed at the following frequency:

1.1.1 For the analysis of pesticide/PCB TCL compounds, a method blank analysis must be performed once:

- each Case, OR
- each 14 calendar day period during which samples in a Case are received (said period beginning with the receipt of the first sample in that Sample Delivery Group), OR
- each 20 samples in a Case, including matrix spike and reanalyses that are of similar matrix (water or soil) or similar concentration (soil only), OR
- whenever samples are extracted by the same procedure (separatory funnel or continuous extraction),

whichever is most frequent, on each GC/MS or GC system used to analyze samples.

1.2 It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

1.2.1 For the purposes of this protocol, an acceptable laboratory method blank should meet the criteria of paragraph 1.2.1.1.

1.2.1.1 The method blank must contain less than or equal to the Contract Required Quantitation Limit of any single pesticide/PCB Target Compound (Exhibit C).

1.2.2 If a laboratory method blank exceeds these criteria, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) MUST be reextracted and reanalyzed at no additional cost to the Agency. The Laboratory Manager, or his designee, must address problems and solutions in the Case Narrative (Exhibit B).

1.3 Documentation

The Contractor shall report results of method blank analysis using the Organic Analysis Data Sheet (Form I). In addition, the samples associated with each method blank must be summarized on Form IV (Method Blank Summary). Detailed instructions for the completion of these forms can be found in Exhibit B, Section III.

1.3.1 The Contractor shall report ALL sample concentration data as UNCORRECTED for blanks.

PART 2 - SURROGATE SPIKE (SS) ANALYSIS

2. Summary

Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before purging or extraction in order to monitor preparation and analysis of samples.

2.1 Each sample, matrix spike, matrix spike duplicate, and blank are spiked with surrogate compounds prior to extraction. The surrogate spiking compounds shown in Table 4.1 are used to fortify each sample, matrix spike, matrix spike duplicate, and blank with the proper concentrations. Performance based criteria are generated from laboratory results. Therefore, deviations from the spiking protocol will not be permitted.

TABLE 4.1. SURROGATE SPIKING COMPOUND

Compound	Fraction	Amount in Sample Extract* (before any optional dilutions) Water	Low/Medium Soil
Dibutylchlorendate	Pest.	0.1 ug	0.1 ug

* At the time of injection.

2.2 Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the advisory recovery limits listed in Table 4.2.

TABLE 4.2. ADVISORY SURROGATE SPIKE RECOVERY LIMITS

Fraction	Surrogate Compound	Water	Low/Medium Soil/Sediment
Pest.	Dibutylchlorendate	(24-154)*	(20-150)*

* These limits are for advisory purposes only. They are not used to determine if a sample should be reanalyzed. When sufficient data becomes available, the USEPA may set performance based contract required windows.

2.3 Documentation

The Contractor shall report surrogate recovery data for the following:

- o Method Blank Analysis
- o Sample Analysis
- o Matrix Spike/Matrix Spike Duplicate Analyses

The surrogate spike recovery data is summarized on the Surrogate Spike Percent Recovery Summary (Form II). Detailed instructions for the completion of Form II are in Exhibit B, Section III.

PART 3 - MATRIX SPIKE/MATRIX SPIKE DUPLICATE ANALYSIS (MS/MSD)

3. Summary

In order to evaluate the matrix effect of the sample upon the analytical methodology, the USEPA has developed the standard mixes listed in Table 5.1 to be used for matrix spike and matrix spike duplicate analyses. These compounds are subject to change depending upon availability and suitability for use as matrix spikes.

3.1 MS/MSD Frequency of Analysis

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

- o each Case of field samples received, OR
- o each 20 field samples in a Case, OR
- o each group of field samples of a similar concentration level (soils only), OR

- each 14 calendar day period during which field 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.

3.2 Use the compounds listed in Table 5.1 to prepare matrix spiking solutions according to protocols described in Exhibit D PEST. The analytical protocols in Exhibit D PEST stipulate the amount of matrix spiking solution to be added to the sample aliquots prior to extraction. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate samples.

TABLE 5.1. MATRIX SPIKING SOLUTIONS

Pesticides	
Heptachlor	Lindane
Aldrin	Endrin
Dieldrin	4,4'-DDT

3.2.1 Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

3.3 Individual component recoveries of the matrix spike are calculated using Equation 5.1.

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100 \qquad \text{Eq. 5.1}$$

where

SSR = Spike Sample Results

SR = Sample Result

SA = Spike Added from spiking mix

3.4 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 5.2.

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100 \qquad \text{Eq. 5.2}$$

where

RPD = Relative Percent Difference

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

3.5 Documentation

The matrix spike (MS) results (concentrations) for nonspiked pesticide/PCB TCL compounds shall be reported on Form I (Organic Analysis Data Sheet) and the matrix spike percent recoveries shall be summarized on Form III (MS/MSD Recovery). These values will be used by EPA to periodically update existing performance based QC recovery limits (Table 5.2).

The results for nonspiked pesticide/PCB TCL compounds in the matrix spike duplicate (MSD) analysis shall be reported on Form I (Organic Analysis Data Sheet) and the percent recovery and the relative percent difference shall be summarized on Form III (MS/MSD Recovery). The RPD data will be used by EPA to evaluate the long term precision of the analytical method. Detailed instructions for the completion of Form III are in Exhibit B, Section III.

TABLE 5.2. MATRIX SPIKE RECOVERY LIMITS*

Fraction	Matrix Spike Compound	Water	Soil/Sediment
Pest.	Lindane	56-123	46-127
Pest.	Heptachlor	40-131	35-130
Pest.	Aldrin	40-120	34-132
Pest.	Dieldrin	52-126	31-134
Pest.	Endrin	56-121	42-139
Pest.	4,4'-DDT	38-127	23-134

* These limits are for advisory purposes only. They are not to be used to determine if a sample should be reanalyzed. When sufficient multi-lab data are available, standard limits will be calculated.

PART 4 - PESTICIDE QA/QC REQUIREMENTS

4. Summary

Part 4 summarizes ongoing QC activities involved with pesticide/PCB analysis that were detailed in Parts 1, 2 and 3 of this Section, and describes the additional QA/QC procedures required during the analysis of pesticide/PCBs that are not covered in Parts 1, 2, and 3.

4.1 The Contractor must perform the following:

4.1.1 Method Blank analysis as per Part 1 of this Section.

4.1.2 Spike all standards, samples, blanks, matrix spike and matrix spike duplicate samples with the surrogate spike compound (dibutylchlorendate) as per Part 2 of this Section.

4.1.3 Matrix Spike/Matrix Spike duplicate analysis as per Part 3 of this Section.

4.2 The external standard quantitation method must be used to quantitate all pesticides/PCBs. Before performing any sample analysis, the laboratory is required to determine the retention time window for each pesticide/PCB target compound listed in Exhibit C and the surrogate spike compound, dibutylchlorendate. These retention time windows are used to make tentative identification of pesticides/PCBs during sample analysis.

4.2.1 Prior to establishing retention time windows, the GC operating conditions (oven temperature and flow rate) must be adjusted such that 4,4'-DDT has a retention time of $\geq$ 12 minutes on packed GC columns, except on OV-1 or OV-101 columns. Conditions listed in Table 7, Exhibit D PEST, Section IV may be used to achieve this criteria.

4.2.2 Establish retention time windows as follows:

4.2.2.1 At the beginning of the contract and each time a new GC column is installed, make three injections of all single component pesticides mixtures, multi-response pesticides, and PCBs throughout the course of a 72-hour period. The concentration of each pesticide/PCB should be sufficient to provide a response that is approximately half scale. The three injections of each compound should be made at approximately equal intervals during the 72-hour period, (e.g., each compound should be injected near the beginning, near the middle, and near the end of the 72-hour period).

4.2.2.2 Verify the retention time shift for dibutylchlorendate in each standard. The retention time shift between the initial and subsequent standards must be less than 2.0% difference for packed columns, less than 1.5% difference for wide bore capillary columns (ID greater than 0.32 mm), and less than 0.3% difference for narrow bore capillary columns (ID less than 0.32 mm). If this criterion is not met, continue injecting replicate standards to meet this criterion.

4.2.2.3 Calculate the standard deviation of the three absolute retention times for each single component

pesticide. For multiresponse pesticides or PCBs, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak.

4.2.2.4 The standard deviations determined in 4.2.2.3 shall be used to determine the retention time windows for a particular 72-hour sequence. Apply plus or minus three times the standard deviations in 4.2.2.3 to the retention time of each pesticide/PCB determined for the first analysis of the pesticide/PCB standard in a given 72 hour analytical sequence. This range of retention times defines the retention time window for the compound of interest for that 72-hour sequence. NOTE: By definition, the retention time of a pesticide/PCB from the first analysis of that compound in the 72 hour sequence is the center of the retention time window. Do not use the retention time measured in 4.2.2.1 as the center of the retention time window. The experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse pesticide/PCBs, the analyst should utilize the retention time window but should primarily rely on pattern recognition.

For example, the three injections of aldrin in 4.2.2.1 have a mean retention time of 1.40 minutes and a standard deviation of 0.01 minutes. The retention time of the aldrin standard at the beginning of the 72-hour sequence begun today is 1.51 minutes. Three times the standard deviation (0.01) is applied to the retention time of aldrin from the sequence begun today, e.g., $1.51 \pm 3(0.01) = 1.48\text{-}1.54$. If aldrin has a retention time of 1.60 minutes at the beginning of the next 72-hour sequence, then the retention time window becomes: $1.60 \pm 3(0.01) = 1.57\text{-}1.63$ for that 72-hour sequence.

4.2.2.5 In those cases where the retention time window for a particular pesticide/PCB is less than 0.01 minutes, the laboratory may substitute whichever of the following formulae apply.

- For packed columns, the retention time window of the particular pesticide/PCB shall be calculated as $\pm$ 1% of the initial retention time of the compound in the 72-hour sequence.

- For wide bore capillary columns (ID greater than 0.32 mm), the retention time window of the particular pesticide/PCB shall be calculated as $\pm$ 0.75% of the initial retention time of the compound in the 72-hour sequence.

- For narrow bore capillary columns (ID less than 0.32 mm), the retention time window of the particular pesticide/PCB shall be calculated as ± 0.15% of the initial retention time of the compound in the 72-hour sequence.

4.2.2.6 Regardless of whether the retention time windows are calculated by the method in 4.2.2.4 or 4.2.2.5, the retention time windows must be reported as a range of values, not as, for example, 1.51 minutes ± 1%.

4.2.2.7 The laboratory must calculate retention time windows for each pesticide/PCB on each GC column used at the beginning of the program and whenever a new GC column is installed. The data must be retained by the laboratory and made available during an on-site laboratory evaluation.

4.3 Primary GC Column Analysis

4.3.1 Primary Analysis establishes whether or not pesticides/PCBs are present in the sample, and establishes a tentative identification of each compound. Quantitation may be performed on the primary analysis if the analysis meets all of the QC criteria specified for quantitation. NOTE: To determine that no pesticides/PCBs are present at or above the contract required quantitation limit is a form of quantitation.

4.3.2 Separation should be ≥ 25 percent resolution between peaks. This criteria must be considered when determining whether to quantitate on the Primary Analysis or the Confirmation Analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

4.3.3 Evaluation Standard Mixtures

4.3.3.1 Prepare Evaluation Standard Mixes A, B, and C (Aldrin, Endrin, 4,4'-DDT and Dibutylchlorendate) at the 3 concentration levels described in Exhibit D PEST. Analyze the three Evaluation Standard Mixes sequentially at the beginning of each seventy-two (72) hour period (See Figure 4.1).

4.3.3.2 Calculate the Calibration Factor (ratio of the total area to the mass injected) for each compound in Evaluation Standard Mix A, B and C using Equation 4.1.

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak}}{\text{Mass Injected (in nanograms)}} \qquad \text{Eq.4.1}$$

4.3.3.3 Using the Calibration Factors from 4.3.3.2 above, calculate the percent relative standard deviation (%RSD) for each compound at the three concentration levels using Equation 4.2. The percent relative standard deviation for Aldrin, Endrin, and Dibutylchlorendate must be less than or equal to 10.0 percent. If the %RSD exceeds 10.0% for 4,4'-DDT, see Section 4.5.4.4.

Note: The 10.0% RSD linearity criteria pertains only to columns being used for Pesticide/PCB quantitation. If a column is used only for surrogate quantitation, the 10.0% RSD is only required for Dibutylchlorendate.

$$\%\ \text{Relative Standard Deviation} = \frac{SD}{\bar{x}} \times 100 \qquad \text{Eq. 4.2}$$

where Standard Deviation (SD) $= \sqrt{\sum_{i-1}^{N} \frac{(x_i - \bar{x})^2}{N-1}}$

$\bar{x}$ = mean of initial three Calibration Factors (per compound).

4.3.3.4 Evaluate the chromatogram from the analysis of the Evaluation Mix B. The appearance of peaks in addition to the four main pesticide peaks indicates a breakdown of Endrin and/or 4,4'-DDT.

4.3.3.5 Calculate the percent breakdown for Endrin and/or 4,4'-DDT on the mixed phase (1.5% OV-16/1.95% OV-210 or equivalent) GC column using Equations 4.3 and 4.4. The percent breakdown for Endrin or 4,4'-DDT must not exceed 20.0 percent. Corrective action must be taken before analysis continues.

$$\%\ \text{breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area}^1\text{(DDE + DDD)}}{\text{Total DDT peak area}^1\text{ (DDT + DDE + DDD)}} \times 100 \qquad \text{Eq. 4.3}$$

$$\%\ \text{breakdown for Endrin} = \frac{\text{Total Endrin degradation peak areas}^1\text{ (Endrin Aldehyde + Endrin Ketone)}}{\text{Total Endrin Peak Area}^1\text{(Endrin + Endrin Aldehyde + Endrin Ketone)}} \times 100 \qquad \text{Eq. 4.4}$$

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[1] The term peak height may be substituted for the term peak area.

4.3.3.6 Calculate the percent breakdown for Endrin and/or 4,4'-DDT on the OV-1 or equivalent GC column using Equations 4.3 and 4.4 The percent breakdown for Endrin or 4,4'-DDT must not exceed 20.0 percent. Corrective action must be taken before analysis continues.

4.3.3.7 If there is evidence of a peak at the retention time for Endrin aldehyde/4,4'-DDD (which coelute on the OV-1 or equivalent GC column), calculate a combined percent breakdown for Endrin/4,4'-DDT using Equation 4.5. The combined Endrin/4,4'-DDT percent breakdown must not exceed 20.0 percent, else corrective action must be taken before analysis continues.

$$\text{Combined \% breakdown} = \frac{\text{Total Endrin/DDT degradation peak areas}^2 \text{ (DDD, DDE, Endrin Aldehyde, Endrin Ketone)}}{\text{Total Endrin/DDT degradation peak area}^2 \text{ (Endrin, Endrin Aldehyde, Endrin Ketone, DDD, DDE, DDT)}} \times 100 \quad \text{Eq. 4.5}$$

4.3.3.8 Suggested Maintenance

Corrective measures may require any one or more of the following remedial actions:

4.3.3.8.1 Packed columns - For instruments with off-column injection; replace the demister trap, clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Inspect the injection end of the column and remove any foreign material (broken glass from the rim of the column or pieces of septa). Replace the glass wool with fresh deactivated glass wool. Also, it may be necessary to remove the first few millimeters of packing material if any discoloration is noted, also swab out the inside walls of the column if any residue is noted. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described below) and/or repack/replace the column.

4.3.3.8.2 Capillary columns - Clean and deactivate the glass injection port insert or replace with a cleaned and

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2 The term peak height may be substituted for the term peak area.

deactivated insert. Break off the first few inches, up to one foot, of the injection port side of the column. Remove the column and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

4.3.3.8.3 Metal Injector Body - Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsate in the beaker.

Prepare a solution of deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone and hexane. Reassemble the injector and replace the GC column.

4.3.4 Individual Standard Mixtures A and B

4.3.4.1 Prepare Individual Standard Mixtures A and B containing the single component pesticides. These may be divided into the groups suggested in Exhibit D PEST, which are recommended to prevent overlap of compounds on two of the packed columns. One mixture of all of the single component pesticides is acceptable when using capillary column. Prepare separate solutions of all multi-response pesticides and PCBs. (Aroclor 1016 and Aroclor 1260 may be combined in a single mixture.)

4.3.4.2 Analyze Individual Standard Mixtures A and B and all multi-response pesticide/PCBs at the beginning of

each 72 hour period (see Figure 4.1) and analyze Individual Standard Mixtures A and B at the intervals specified in the analytical sequence in Figure 4.1, and whenever sample analysis is completed. The Calibration Factor for each standard quantitated (Individual Standard Mix A or B) (Equation 4.6), must not exceed a 15.0 percent difference for a quantitation run nor exceed a 20.0 percent difference for a confirmation run during the 72 hour period. Calculate percent difference using Equation 4.7. Deviations greater than 15.0 percent require the laboratory to repeat the samples analyzed following the quantitation standard that exceeded the criterion.

NOTE: Aroclors 1221 and 1232 must be analyzed at a minimum of once a month on each instrument and each column. Copies of these chromatograms must be submitted with each case for instruments and columns used to quantitate samples in that case, when identity of these two pesticides (Aroclor 1221 and 1232) has been confirmed.

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak*}}{\text{Mass injected (in nanograms)}} \qquad \text{Eq. 4.6}$$

* For multiresponse pesticides/PCBs use the total area of all peaks used for quantitation.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100 \qquad \text{Eq. 4.7}$$

where

R_1 = Calibration Factor from first analysis

R_2 = Calibration Factor from second or subsequent analysis

4.4 Sample Analysis (Primary GC Column)

4.4.1 Samples are analyzed per the sequence described in Figure 4.1.

4.4.2 The retention time shift for Dibutylchlorendate must be evaluated after the analysis of each sample. The retention time shift must be less than 2.0% difference for packed GC columns between the initial standard analysis and any sample or standard analyzed during the 72 hour period. The percent difference for wide bore capillary columns (ID greater than 0.32 mm) must be less than 1.5%. The percent difference for narrow bore capillary columns (ID less than 0.32 mm) must be less than 0.3% (Equation 4.8).

$$\text{Percent Difference (\%D)} = \frac{RT_I - RT_S}{RT_I} \times 100 \qquad \text{Eq. 4.8}$$

where

RT_I = absolute retention time of Dibutylchlorendate in the initial standard (Evaluation Standard Mix A).

RT_S = absolute retention time of Dibutylchlorendate in the sample or subsequent standard.

4.4.3 Evaluate the GC column throughout the analysis of samples by injecting Evaluation Standard Mix B at the frequency outlined in Figure 4.1.

4.4.4 Calculate the percent breakdown for 4,4'-DDT and Endrin according to 4.3.3.5. Take corrective action when the breakdown for 4,4'-DDT or Endrin exceeds 20.0 percent.

FIGURE 4.1 72 HOUR SEQUENCE FOR PESTICIDE/PCB ANALYSIS

1. Evaluation Standard Mix A
2. Evaluation Standard Mix B
3. Evaluation Standard Mix C
4. Individual Standard Mix A*
5. Individual Standard Mix B*
6. Toxaphene
7. Aroclors 1016/1260
8. Aroclor 1221**
9. Aroclor 1232**
10. Aroclor 1242
11. Aroclor 1248
12. Aroclor 1254
13. 5 Samples
14. Evaluation Standard Mix B
15. 5 Samples
16. Individual Standard Mix A or B
17. 5 Samples
18. Evaluation Standard Mix B
19. 5 Samples
20. Individual Standard Mix A or B (whichever not run in step 16)
21. 5 Samples
22. Repeat the above sequence starting with Evaluation Standard Mix B (step 14 above).
23. Pesticide/PCB analysis sequence must end with the analysis of <u>both</u> Individual Standard Mix A <u>and</u> B regardless of number of samples analyzed.

* These may be one mixture.

** Aroclors 1221 and 1232 must be analyzed at a minimum of <u>once per month</u> on each instrument and each column. Copies of these chromatograms must be submitted with each Case for instruments and columns used to quantitate samples in that Case.

4.4.5 If one or more compounds have a response greater than full scale, the extract requires dilution according to the specifications in Exhibit D PEST. If the dilution of the extract causes any compounds tentatively identified in the first analysis to be undetectable in the second analysis, then the results of both analyses shall be reported on separate Forms I, according to the instructions in Exhibit B. For dilutions greater than 10-fold, also see the instructions in Exhibit D PEST.

4.5 Confirmation Analysis (GC/EC)

4.5.1 Confirmation Analysis is to confirm the presence of all compounds tentatively identified in the Primary Analysis. Therefore, the only standards that are required are the Evaluation Standard Mixes (to check linearity and degradation criteria) and standards of all compounds to be confirmed. The 72-hour sequence described in Figure 4.1 is, therefore, modified to fit each case. Quantitation may be performed on the confirmation analysis. If toxaphene or DDT is to be quantitated, additional linearity requirements are specified in Section 4.5.4.

4.5.2 Separation should be > 25 percent resolution between peaks. This criteria must be considered when determining whether to quantitate on the Primary Analysis or the Confirmation Analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

4.5.2.1 For a fused silica capillary (FSCC) confirmation, there must be > 25 percent resolution (valley) between the following pesticide pairs:

- beta-BHC and delta-BHC
- Dieldrin and 4,4'-DDT
- 4,4'-DDD and Endrin Aldehyde
- Endosulfan Sulfate and 4,4'-DDT

4.5.3 All QC specified previously must be adhered to, i.e., the ≥ 12 minutes retention time for 4,4'-DDT, and the specified criteria for 4,4'-DDT and endrin degradation, linearity, calibration factor for standards, and retention time shift for dibutylchlorendate. The retention time requirement 4,4'-DDT does not have to be met if the confirmation column is OV-1 or OV-101.

4.5.4 Begin the Confirmation Analysis GC sequence with the three concentration levels of Evaluation Standard Mixes A, B and C. The exception to this occurs when toxaphene and/or DDT series are to be confirmed and quantitated. There are four combinations of pesticides that could occur, therefore, the

following sequences must be followed depending on the situation.

4.5.4.1 Toxaphene only - Begin the sequence with Evaluation Mix B to check degradation, followed by three concentration levels to toxaphene. Check linearity by calculating %RSD. If ≤ 10.0% RSD, use the appropriate equation in Exhibit D PEST for calculation. If >10.0% RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

4.5.4.2 DDT, DDE, DDD only - Begin the sequence with Evaluation Mix B. Then inject three concentration levels of a standard containing DDE, DDD and DDT. Calculate linearity and follow the requirements specified in 4.5.4.1 for each compound to be quantitated.

4.5.4.3 DDT series and toxaphene - Begin the sequence with Evaluation Mix B. Then inject three concentration levels of toxaphene and another three levels of the DDT series. Calculate linearity and follow the requirements specified in 4.5.4.1 for each compound to be quantitated.

4.5.4.4 Other pesticides/PCBs plus DDT series and/or toxaphene Begin the sequence with Evaluation Standard Mixes A, B and C. Calculate linearity on the four compounds in the Evaluation Standards mixes. If DDT and/or one or more of the other compounds are >10.0% RSD and/or degradation exceeds the criterion, corrective maintenance as outlined in paragraph 4.3.3.8 should be performed before repeating the above chromatography evaluations. If DDT only exceeds the linearity criteria and one or more of the DDT series is to be quantitated, follow 4.5.4.2 (do not repeat Evaluation Mix B). If none of the DDT series is to be quantitated and DDT exceeds the 10.0% RSD, simply record the % RSD on the proper form. Anytime toxaphene is to be quantitated, follow 4.5.4.1.

4.5.5 After the linearity standards required in 4.5.4 are injected, continue the confirmation analysis injection sequence with all compounds tentatively identified during primary analysis to establish the daily retention time windows during primary analysis. Analyze all confirmation standards for a case at the beginning, at intervals specified in 4.5.6, and at the end. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The laboratory must reanalyze all samples between the standard that exceeds the criterion and a subsequent standard that meets the criterion.

4.5.6 Begin injection of samples at this point of the Confirmation Analysis sequence. Analyze groups of 5 samples with a standard pertaining to the samples after each group (Evaluation Mix B is required after the first 5 samples, and every 10 samples thereafter, e.g., after 5, 15, 25, etc). The alternating standard's calibration factors must be within 15.0 percent of each other if quantitation is performed. Deviations larger than 15.0 percent require the laboratory to repeat the samples analyzed between the standard that exceeds the criterion and a subsequent standard that meets the criterion. The 15.0 percent criterion only pertains to compounds being quantitated.

4.5.6.1 If more than one standard is required to confirm all compounds tentatively identified in the Primary Analysis, include an alternate standard after each 10 samples.

4.5.6.2 Samples must also be repeated if the degradation of either DDT and/or Endrin exceed 20.0 percent on the intermittent Evaluation Standard Mix B.

4.5.6.3 If the samples are split between 2 or more instruments, all standards and blanks pertaining to those samples must be analyzed on each instrument.

4.5.7 Inject the method blanks (extracted with each set of samples) on every GC and GC column on which the samples are analyzed.

4.5.8 If quantitation is performed on the confirmation analysis, follow the instructions in 4.4.5 regarding dilution of extracts and reporting results.

4.6 GC/MS Pesticide/PCB Confirmation

4.6.1 Any pesticide/PCB confirmed by two dissimilar GC columns must also be confirmed by GC/MS if the concentration in the final sample extract is sufficient for GC/MS analysis (based on laboratory GC/MS detection limits).

4.6.1.1 Pesticides/PCBs may be confirmed utilizing the extract prepared for semivolatile GC/MS analysis; however, the absence of pesticide/PCBs in the semivolatile extract would require the analysis of the pesticide/PCB (fraction) extract.

4.6.2 The tuning and mass calibration criteria for DFTPP (50 ng) MUST be met prior to any confirmation of pesticides/PCBs is undertaken. Refer to the tuning and mass calibration instruction for semivolatiles. The characteristic ions for GC/MC analysis of pesticides/PCBs are given in Exhibit D SV, Table 5.

4.6.3 The pesticide/PCB sample extract(s) and the associated pesticide/PCB blank(s), and reference standard(s) must be analyzed by GC/MS.

4.7 Documentation

See Exhibit B for complete instructions for the completion of all required forms and the Deliverable Index for all reporting and deliverables requirements.

TITLE: PNL-ALO-347, SAMPLE PREPARATIONS FOR PESTICIDES/PCBs ANALYSIS IN WATER AND SOIL/SEDIMENT

APPLICABILITY

This procedure applies to preparation of water and soil/sediment samples for analysis of pesticide and PCB compounds by Procedure PNL-ALO-346. It includes extraction and cleanup of water and low and medium level soil/sediment samples. Water samples are extracted by a continuous liquid-liquid extractor or by separatory funnel shake-out into methylene chloride, the methylene chloride is evaporated, and the residue is dissolved in hexane. An alumina chromatographic column is used for the sample cleanup, and the sample is diluted to volume for the gas chromatographic (GC) analysis. Soil/sediment samples are extracted into hexane for the medium level samples and into methylene chloride/acetone for the low level samples using sonication for the agitation. These extracts are then cleaned up and prepared for the GC analysis.

DEFINITIONS

N/A

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

QUALITY CONTROL

Sample preparation steps that support the quality control requirements for the analysis, method PNL-ALO-346, are included in this procedure.

PROCEDURE

1.0 Sample Storage and Holding Times

1.1 Procedures for Sample Storage

1.1.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until extraction and analysis.

Author / Date	Project Mgr. / Date	PQ Representative / Date
RW Stromatt 1-8-93	TY Hosaka 3/11/93	TL Ehlert 3/3/93
Technical Reviewer / Date	**Line Mgr. / Date**	**Other / Date**
EW Hoppe 2-14-93	AG King for HK 3/2/93	

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1.1.2 After analysis, extracts and unused sample volume must be protected from light and refrigerated at 4°C (±2°C) for the periods specified in the contract schedule.

1.2 Contract Required Holding Times

1.2.1 If separatory funnel or sonication procedures are employed for extractions for pesticide/PCB analyses, extraction of water samples shall be completed within 5 days of Validated Time of Sample Receipt (VTSR), and extraction of soil/sediment samples shall be completed within 10 days of VTSR. If continuous liquid-liquid extraction procedures are employed, extraction of water samples shall be started within 5 days of VTSR.

1.2.2 Extracts of either water or soil/sediment samples must be analyzed within 40 days following extraction.

2.0 Sample Preparation for Pesticides/PCBs in Water

2.1 Summary of Method

A measured volume of sample, approximately 1 L, is solvent extracted with methylene chloride using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, exchanged to hexane and adjusted to a final volume of 10 mL. Radioactive samples may have less volume because of availability and dose rate.

2.2 Interferences/Tolerance

2.2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as broad eluting peaks. Common flexible plastics contain varying amounts of phthlates. These phthalates are easily extracted or leached form such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory.

Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

2.2.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the site being sampled. The cleanup procedures in paragraphs 2.7.1 through 2.7.5 must be used to overcome such interferences to attempt to achieve the Contract Required Quantitation Limit (CRQLs). The cleanup procedures in paragraph 2.8.1 through 2.8.5 may be used to remove sulfur interferences.

2.2.3 Unless otherwise stated tolerances for all values given within this method are to within the first, non-zero, significant integer, including the number 10, that is specified. For example, 5 mL implies accuracy to within ±1 mL, while 5.0 mL implies accuracy within ±0.1 mL. If 100 mL is specified, it implies accuracy to ±1 mL.

When preparing samples and standards and making standard spike addition, the volumes specified shall be measured to that value using the specified or appropriate measuring device. For example, if 1 L water sample is specified to be measured in a 1 L graduated cylinder, the water sample is added to the 1000 mL mark: if 7.5 µL is specified, a 10 µL gas tight syringe is filled to the 7.5 µL mark: if 30 µL is specified, a 50 µL gas tight syringe is filled to the 30 µL mark. Manufacturer tolerances are acceptable for the specified volumetric measurements in this procedure.

2.3 Apparatus and Materials

2.3.1 Glassware (brand names and catalog numbers included for illustration purposes only).

2.3.1.1 Separatory funnel, 2000 mL with Teflon stopcock.

2.3.1.2 Drying column, Chromatographic column approximately 400 mm long X 19 mm ID, with coarse frit. (Substitution of a small pad of disposable Pyrex glass wool for the frit will help prevent cross-contamination of sample extracts.)

2.3.1.3 Concentrator tube, Kuderna-Danish (K-D), 10 mL, graduated (Kontes K-570050-1025 or equivalent). Ground glass stopper is used to prevent evaporation of extracts.

2.3.1.4 Evaporative flask, K-D, 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

2.3.1.5 Snyder column, K-D, three-ball macro (Kontes K-503000-0121 or equivalent).

2.3.1.6 Snyder column, K-D, two-ball micro (Kontes K-569001-0219 or equivalent).

2.3.1.7 Continuous liquid-liquid extractors, equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor-Ace Glass Company, Vineland, NJ P/N 6841-10, or equivalent.)

2.3.1.8 Vials, amber glass, 10 to 15 mL capacity, with Teflon-lined screw cap.

2.3.1.9 Bottle or test tube, 50 mL with Teflon-lined screw cap for sulfur removal.

2.3.1.10 Chromatographic column for alumina, 8 mL (200 mm X 8 mm ID) polypropylene column (Kontes K-420160 or equivalent) or 6 mL (150 mm X 8 mm ID) glass column (Kontes K-420155 or equivalent or 5 mL serological pipettes plugged with a small piece of Pyrex glass wool in the tip. The Kontes columns may be plugged with Pyrex glass wool or a polyethylene porous disk (Kontes K-420162).

2.3.2 Pyrex glass wool, pre-rinse glass wool with appropriate solvents to ensure its cleanliness.

2.3.3 Silicon carbide boiling chips, approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

2.3.4 Water bath, heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

2.3.5 Balance, analytical, capable of accurately weighing ±0.0001 g.

2.3.6 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc., South Berlin, MA (or equivalent) is suitable.

2.4 Reagents

2.4.1 Reagent water, reagent water is defined as a water in which an interferant is not observed at or above the CRQL of each parameter of interest.

2.4.2 Acetone, hexane, isooctane (2,2,4-trimethylpentane), methylene chloride Pesticide quality or equivalent.

2.4.3 Sodium sulfate, reagent grade, granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray.

2.4.4 Alumina, neutral, Super I Woelm (Universal Scientific, Incorporated, Atlanta, Georgia) or equivalent. Add 7% (v/w) reagent water to the Super I neutral alumina. Tumble or shake in a wrist action shaker for a minimum of two hours or preferably overnight. There should be no lumps present. Store in a tightly sealed glass container. A 25 cycle soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide technique indicates any interferences for the compounds of interest.

2.4.4.1 Alumina Equivalency Check. Test the alumina by adding the BNA surrogates (see method PNL-ALO-345) in 1:1 acetone/hexane to the alumina and following paragraph 2.7.1. The tribromophenol should not be detected by GC/EC if the alumina and its activation are acceptable. Also check recovery of all single component pesticides following the same procedure. The percent recovery for all single component pesticides must be ≥80%, except for endosulfan sulfate which must be ≥60% and endrin aldehyde which is not recovered. The data must be retained by the laboratory and made available for inspection during on-site evaluations. If the alumina deactivated with 7% (v/w) reagent water does not prove adequate to remove the BNA surrogates and other interferences, the alumina may be deactivated with as much as 9% reagent water, so long as the criteria for tribromophenol and the recovery of all single component pesticides can be met.

2.4.5 Sodium hydroxide solution (10N)-(ACS). Dissolve 40 g reagent grade NaOH in reagent water and dilute to 100 mL.

2.4.6 Tetrabutylammonium (TBA) - Sulfite reagent. Dissolve 3.39 g TBA hydrogen sulfate in 100 mL distilled water. To remove impurities, extract this solution three times

with 20 mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw cap. This solution can be stored at room temperature for at least one month.

2.4.7 Pesticide surrogate standard spiking solution.

2.4.7.1 The surrogate standard is added to all samples and calibration solutions; the compound specified for this purpose is dibutylchlorendate.

2.4.7.2 Prepare a surrogate standard spiking solution at a concentration of 1 μg/1.00 mL in acetone. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with quality control check samples indicates a problem.

2.4.8 Sulfuric acid solution (1+1)-(ACS). Slowly, add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

2.4.9 Pesticide matrix standard spiking solution. Prepare a spiking solution of acetone or methanol that contains the following pesticides in the concentrations specified.

PESTICIDE	μg/1.0 mL
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4' DDT	0.5

Matrix spikes are also to serve as duplicates by spiking two 1 L portions from the one sample chosen for spiking.

2.4.10 See method PNL-ALO-346, pages 19-35, for contract-required quality assurance/quality control procedures.

2.5 Sample Extraction - Separatory Funnel

2.5.1 Samples may be extracted using separatory funnel techniques. If emulsions prevent acceptable solvent recovery with separatory funnel extractions, continuous liquid-liquid extraction (section 2.6) may be used. The separatory funnel extraction scheme described below assumes a sample volume of

the 1 L. Continuous extraction is recommended for extraction of radioactive samples to minimize analyst contact. Sample volumes of less then 1 L may be necessary because of availability and dose rate.

2.5.2 Using a 1 L graduated cylinder, measure out a 1 L sample aliquot and place it into a 2 L separatory funnel. Check the pH of the sample with wide range pH paper and adjust to between 5 and 9 pH with 10 N sodium hydroxide and/or 1:1 sulfuric acid solution.

NOTE: Recovery of dibutylchlorendate will be low if pH is outside this range. Alpha-BHC, gamma-BHC, Endosulfan I and II and Endrin are subject to decomposition under alkaline conditions, and therefore, may not be detected if the pH is above 9.) Pipet 1.0 mL surrogate standard spiking solution into the separatory funnel and mix well. Add 1.0 mL of pesticide matrix spiking solution to each of two 1 L portions from the sample selected for spiking.

2.5.3 Add 60 mL methylene chloride to the separatory funnel and extract the sample by shaking the funnel for two minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume 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 means. Drain methylene chloride into a 250 mL Erlenmeyer flask.

2.5.4 Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

2.5.5 Assemble a K-D concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all pesticides shown in Target Compound List table in PNL-ALO-346.

2.5.6 Pour the combined extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate, and collect the extract in the K-D concentrator. Rinse the

Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

2.5.7 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding an apparent volume of 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 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 15 minutes. A longer period of time for the concentration may be required if the temperature is maintained 90°C or less and if the concentration process is preformed in a high air flow radiochemistry hood. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes.

2.5.8 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip and re-attach the Snyder column. Pre-wet the column by adding an apparent volume of 1 mL of hexane to the top. Concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. A longer period of time for the concentration may be required if the temperature is maintained 90°C or less and if the concentration process is preformed in a high flow radiochemistry hood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool at least 10 minutes.

2.5.9 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. If sulfur crystals are a problem, proceed to paragraph 2.8.1; otherwise continue to paragraph 2.5.10, or use the micro-Snyder column technique (see section 2.5.9 in Procedure PNL-ALO-344).

2.5.10 Nitrogen blowdown technique (taken from ASTM Method D 3086)

Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to approximately 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). **CAUTION:** New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of the

tube must be rinsed down several times with hexane during the operation and the final volume brought to 0.5 mL. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

2.5.11 Dilute the extract to 1 mL with acetone and proceed to paragraph 2.7.1 (Alumina Column Cleanup).

2.6 Sample Extraction - Continuous Liquid-Liquid Extractor

2.6.1 When experience with a sample from a given source indicates that a serious emulsion problem will result, or if an emulsion is encountered in paragraph 2.5.3 using a separatory funnel, a continuous extractor should be used. Continuous extraction is also recommended for radioactive samples.

2.6.2 Using a 1 L graduated cylinder, measure out a 1 L sample aliquot and place it into the continuous extractor. Pipet 1.0 mL surrogate standard spiking solution into the continuous extractor and mix well. Check the pH of the sample with wide range pH paper and adjust to between 5 and 9 pH with 10N sodium hydroxide and/or 1:1 sulfuric acid solution. Radioactive sample volume of less than 1 L may be necessary because of availability and dose rate.

2.6.3 Add 500 mL of methylene chloride to the distilling flask. Add sufficient reagent water to ensure proper operation and extract for 18 hours. Allow to cool, then detach the boiling flask and dry. Concentrate the extract as in paragraphs 2.5.5 through 2.5.11.

2.7 Alumina Column Cleanup

2.7.1 Add 3 g of activity III neutral alumina to the 10 mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

2.7.2 Transfer the 1 mL of hexane/acetone extract from paragraph 2.5.11 to the top of the alumina using a disposable Pasteur pipet. Collect the eluate in a clean 10 mL concentrator tube.

2.7.3 Add 1 mL of hexane to the original extract concentrator tube to rinse it. Transfer these rinsings to the alumina column. Elute the column with an additional 9 mL of hexane. Do not allow the column to go dry during the additional and elution of the sample.

2.7.4 Adjust the extract to a final volume of 10 mL using hexane.

2.7.5 The pesticide/PCB fraction is ready for analysis. Proceed to method PNL-ALO-346. Store the extracts at 4°C (±2°C) in the dark in Teflon-sealed containers until analyses are performed.

2.8 Optional Sulfur Cleanup

2.8.1 Concentrate the hexane extract from paragraph 2.5.9 to 1 mL.

2.8.2 Transfer the 1 mL to a 50 mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1 mL of hexane, adding the rinsings to the 50 mL bottle.

2.8.3 Add 1 mL TBA-sulfite reagent and 2 mL 2-propanol, cap the bottle, and shake for at least 1 minute. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100 mg portions until a solid residue remains after repeated shaking.

2.8.4 Add 5 mL distilled water and shake for at least 1 minute. Allow the sample to stand 5 to 10 minutes. Transfer the hexane layer (top) to a concentrator ampule and go back to paragraph 2.5.10.

3.0 Protocols For Soil/Sediment

It is mandatory that all soil/sediment samples be characterized as to concentration level so that the appropriate analytical protocol may be chosen to ensure proper quantitation limits for the sample.

The use of GC/EC methods is recommended for screening soil/sediment samples for pesticides/PCBs, however, the cognizant scientist is at liberty to determine the specific method of characterization.

Note that the terms "low level" and "medium level" are not used here as a judgement of degree of contamination but rather as a description of the concentration ranges that are encompassed by the "low" and "medium" level procedures.

The concentration range covered by the low level analysis may be considered to be less than 1000 µg/kg of pesticides/PCBs. The concentration range covered by the medium level analysis is greater than 1000 µg/kg.

3.1 Medium Level Preparation of Analysis of Pesticides/PCBs in Soil/Sediment

3.1.1 Scope and Application

This procedure is designed for the preparation of sediment/soil samples which may contain pesticides/PCBs at a level greater than 1000 µg/kg.

3.1.1.1 If the extract for pesticide/PCB analysis is to be prepared from an aliquot of the semi-volatile extract, also refer to the specific instructions in method PNL-ALO-344, section 2.2.7.1.

3.1.2 Summary of Method

3.1.2.1 Portions of soil/sediment are extracted and screened by methods of the cognizant scientist's choice.

3.1.2.2 If pesticides/PCBs are detected in the screen at levels above approximately 1000 µg/kg, a 1 g sample is extracted with 10.0 mL of hexane for analysis by GC/EC.

3.1.2.3 If no pesticides/PCBs are detected above 1000 µg/kg, then the sample shall be prepared by the low level protocol.

3.1.3 Interferences

3.1.3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be cause by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

3.1.4 Limitations

3.1.4.1 The procedure is designed to allow quantitation limits as low as 1000 µg/kg for pesticides/PCBs. If peaks are present based on GC screen, the sample is determined to require a medium level analysis by GC/EC. Some samples may contain high concentrations of chemicals that interfere with the analysis of other components at lower

levels; the quantitation limits in those cases may be significantly higher.

3.1.5 Reagents

3.1.5.1 Sodium Sulfate - anhydrous powdered reagent grade, heated at 400°C for four hours, cooled in a desiccator and stored in a glass bottle Baker anhydrous powder, catalog #73898 or equivalent.

3.1.5.2 Methylene chloride. Pesticide residue analysis grade or equivalent.

3.1.5.3 Hexane. Pesticide residue analysis grade or equivalent.

3.1.5.4 Methanol. Pesticide residue analysis grade or equivalent.

3.1.5.5 Acetone. Pesticide residue analysis grade or equivalent.

3.1.5.6 Pesticide/PCB Surrogate Standard Spiking solution.

3.1.5.6.1 The compound specified in dibutylchlorendate. Prepare a solution at a concentration of 20 µg/1.0 mL in methanol. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with quality control check samples indicates a problem.

3.1.5.7 Pesticide/PCB Matrix Standard Spiking solution.

3.1.5.7.1 Prepare a spiking solution in methanol that contains the following pesticides in the concentrations specified below. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with quality control check samples indicates a problem.

PESTICIDE	µg/1.0 mL
Lindane	2.0
Heptachlor	2.0
Aldrin	2.0
Dieldrin	5.0
Endrin	5.0
4,4' DDT	5.0

3.1.5.8 Alumina - neutral, super I Woelm (Universal Scientific, Atlanta, GA) or equivalent. Add 7% (v/w) reagent water to the Super I neutral alumina. Tumble or shake on a wrist action shaker for a minimum of two hours or preferably overnight. There should be no lumps present. Store in a tightly sealed glass container. A 25 cycle soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide techniques indicates any interferences for the compounds of interest.

3.1.5.8.1 Alumina Equivalency Check. Test the alumina by adding the BNA surrogates (see method PNL-ALO-344) in 1:1 acetone/hexane to the alumina and following paragraph 3.2.8.1. The tri-bromophenol should not be detected by GC/EC if the alumina and its activation are acceptable. Also check recovery of all single component pesticides following the same procedure. The percent recovery for all single component pesticides must be ≥80%, except for endosulfan sulfate which must be ≥60% and endrin aldehyde which is not recovered. The data must be retained by the laboratory and made available for inspection during on-site evaluations. If the alumina deactivated with 7% (v/w) reagent water does not prove adequate to remove the BNA surrogates and other interferences, the alumina may be deactivated with as much as 9% reagent water, so long as the criteria for tribromophenol and the recovery of all single component pesticides can be met.

3.1.5.9 Reagent Water - Reagent water is defined as water in which an interference is not observed at or above the CRQL of each parameter of interest.

3.1.6 Equipment

3.1.6.1 Glass scintillation vials, at least 20 mL, with screw cap and Teflon or aluminum foil liner.

3.1.6.2 Spatula. Stainless steel or Teflon.

3.1.6.3 Balance capable of weighing 100 g to the nearest 0.01 g.

3.1.6.4 Vials and caps, 2 mL for GC auto sampler.

3.1.6.5 Disposable pipettes, Pasteur; glass wool rinsed with methylene chloride.

3.1.6.6 15 mL concentrator tubes.

3.1.6.7 Ultrasonic cell disrupter, Heat Systems-Ultrasonics, Inc., Model W-385 SONICATOR (475 Watt with pulsing capability, No. 200 1/2 in. tapped disrupter horn, and No. 419 1/8 in. standard tapered MICROTIP probe), or equivalent device with a minimum of 375 Watt output capability.

NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the MICROTIP probe must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

3.1.6.8 Sonabox acoustic enclosure - recommended with above distributors for decreasing cavitation sound.

3.1.6.9 Test tube rack.

3.1.6.10 Oven, drying.

3.1.6.11 Desiccator.

3.1.6.12 Crucibles, porcelain.

3.1.6.13 Chromatography column for alumina. 8 mL (200 mm & 8 mm ID) Polypropylene column (Kontes K-420160 or equivalent) or 6 mL (150 mm X 8 mm ID) glass column (Kontes K-420155 or equivalent) or 5 mL serological pipettes plugged with a small piece of Pyrex glass wool in the tip. (Pyrex glass wool shall be pre-rinsed with appropriate solvents to insure its cleanliness.) The Kontes columns may be plugged with Pyrex glass wool or a polyethylene porous disk (Kontes K-420162).

3.1.7 Sample Preparation

3.1.7.1 Medium Level preparation for analysis of Pesticide/PCBs.

3.1.7.1.1 Transfer the sample container into a fume hood. Open the sample vial and mix the sample. Transfer approximately 1 g (record weight to nearest 0.1 g) of sample to a 20 mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of the sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

3.1.7.1.1.1 Transfer 50 g of soil/sediment to 100 mL beaker. Add 50 mL of water and stir for one hour. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the cognizant scientist cited in the contract for instructions on how to handle the sample. Document the instructions in the Case Narrative. Discard this portion of sample.

NOTE: Recovery of dibutylchlorendate will be low if pH is outside this range.

3.1.7.1.2 Add at least 2 g of anhydrous powdered sodium sulfate to the sample and mix well.

3.1.7.1.3 Surrogate standards are added to all samples, spikes and blanks. Add 50 µL of surrogate spiking solution to the sample mixture.

3.1.7.1.4 Add 1.0 mL of matrix standard spiking solution to each to two 1 g portions from the sample chosen for spiking.

3.1.7.1.5 Immediately add 10.0 mL (only 9.0 mL for the matrix spike sample) of hexane to the sample and disrupt the sample with the 1/8 in. tapered MICROTIP ultrasonic probe for one minute with the W-385 (or two minutes with the W-375) with output control setting at 5 and mode switch on "1 sec. pulse" and % duty cycle set at 50%. (If using a sonicator other than Models W-375 or W-385, contact the Project Officer for appropriate output settings.) Before extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clear spatula, or very carefully with the tip of the unenergized probe.

3.1.7.1.6 Loosely pack disposable Pasteur pipettes with 2-3 cm glass wool plugs. Filter the extract through the glass wool and collect at approximately 5 mL in a concentrator tube.

3.1.7.1.7 Transfer 1.0 mL of the hexane extract to a glass concentrator tube and concentrate to approximately 0.5 mL using Nitrogen blowdown or the micro-Snyder column technique (per section 2.5.9 in procedure PNL-ALO-344). Add 0.5 mL of acetone to 0.5 mL of hexane extract. Swirl to mix. The pesticide extract must

now be passed through an alumina column to remove polar interferences.

3.1.7.1.8 Follow the procedures for low level soil sediment preparation outlined in paragraphs 3.2.7.1 through 3.2.8.3 for alumina cleanup and sulfur removal.

3.2 Low Level Preparation of Analysis of Pesticides/PCBs in Soil/Sediment

3.2.1 Summary of Method

3.2.1.1 If based on the results of a GC/EC screen, no pesticides/PCBs are present in the sample above 1000 µg/kg, a 30 g portion of soil/sediment is mixed with anhydrous powdered sodium sulfate and extracted with 1:1 methylene chloride/acetone using an ultrasonic probe. The extract is concentrated and an optional gel permeation column cleanup may be used. The extract is cleaned up using a micro alumina column and analyzed by GC/EC for pesticides.

3.2.2 Interferences

3.2.2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

3.2.3 Apparatus and Materials

3.2.3.1 Apparatus for determining percent moisture.

3.2.3.1.1 Oven, drying.

3.2.3.1.2 Desiccator.

3.2.3.1.3 Crucibles, porcelain.

3.2.3.2 Disposable Pasteur glass pipettes, 1 mL.

3.2.3.3 Ultrasonic cell disrupter, Heat Systems - Ultrasonics, Inc., Model W-385 SONICATOR (475 Watt with pulsing capability, No. 305 3/4 in. tapped high gain "Q" disrupter horn or No. 208 3/4 in. standard solid disrupter horn), or equivalent device with a minimum of 375 Watt output capability.

NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the probe must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

3.2.3.3.1 Sonabox acoustic enclosure - recommended with above distributors for decreasing cavitation sound.

3.2.3.4 Centrifuge bottle, heavy wall, 200 mL.

3.2.3.5 Vacuum filtration apparatus.

3.2.3.5.1 Funnel, fluted, 10 cm.

3.2.3.5.2 Filter paper, Whatman No. 41 or equivalent.

3.2.3.6 K-D apparatus.

3.2.3.6.1 Concentrator tube, 10 mL, graduated (Kontes K-570040-1025 or equivalent).

3.2.3.6.2 Evaporative flask, 500 mL (Kontes K-570001-0500 or equivalent).

3.2.3.6.3 Snyder column, three-ball micro (Kontes K-503000-0121 or equivalent).

3.2.3.6.4 Snyder column, two-ball micro (Kontes K-569001-0219 or equivalent).

3.2.3.7 Silicon carbide boiling chips, approximately 10/40 mesh. Heat at 400°C for 30 minutes or Soxhlet extract with methylene chloride.

3.2.3.8 Water bath, heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

3.2.3.9 Balance, capable of accurately weighing ±0.01 g.

3.2.3.10 Vials and caps, 2 mL for GC auto sampler.

3.2.3.11 Balance, analytical, capable of accurately weighing ±0.0001 g.

3.2.3.12 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomatin Associates, Inc., South Berlin, MA (or equivalent) is suitable.

3.2.3.13 Gel permeation chromatography (GPC) cleanup device.

NOTE: GPC cleanup is highly recommended for all extracts for low level soils.

3.2.3.13.1 Automated system

3.2.3.13.1.1 GPC Analytical Biochemical Laboratories, Inc., GPC Autoprep 1002 or equivalent including:

3.2.3.13.1.2 25 mm ID X 600 - 700 mm glass column packed with 70 g of Bio-Beads SX-3.

3.2.3.13.1.3 Syringe, 10 mL with Luer-Lock fitting.

3.2.3.13.1.4 Syringe filter holder and filters, stainless steel and TFE, Gelman 4310 or equivalent.

3.2.3.13.2 Manual system assembled from parts. (Wise, R. H., Bishop, D. F., Williams, R. T., & Austern, B. M. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges" U.S. EPA, Municipal Environmental Research Laboratory, Cincinnati, Ohio 45268.)

3.2.3.13.2.1 25 mm ID X 600 - 700 mm heavy wall glass column packed with 70 g of Bio-Beads SX-3.

3.2.3.13.2.2 Pump, Altex Scientific, Model No. 1001A, or equivalent, semi-preparative, solvent metering system. Pump capacity = 28 mL/minute.

3.2.3.13.2.3 Detector, Altex Scientific, Model No. 153, or equivalent, with 254 nm UV source and 8 μL semi-preparative flowcells (2 mm pathlengths).

3.2.3.13.2.4 Microprocessor/controller, Altex Scientific, Model No. 420, or equivalent, Microprocessor System Controller, with extended memory.

3.2.3.13.2.5 Injector, Altex Scientific, catalog No. 201-56, or equivalent, sample injection valve, Tefzel, with 10 mL sample loop.

3.2.3.13.2.6 Recorder, Linear Instruments, Model No. 385, 10 in. recorder, or equivalent.

3.2.3.13.2.7 Effluent Switching Valve, Teflon slider valve, 3-way with 0.060 in. ports.

3.2.3.13.2.8 Supplemental Pressure Gauge with connecting Tee, U.S. Gauge, 0-200 psi, stainless steel. Installed as a "downstream" monitoring device between column and detector. Flow rate was typically 5 mL/minute of methylene chloride. Recorder chart speed was 0.50 cm/minute.

3.2.3.14 Chromatography column for alumina. 8 mL (200 mm & 8 mm ID) Polypropylene column (Kontes K-420160 or equivalent) or 6 mL (150 mm X 8 mm ID) glass column (Kontes K-420155 or equivalent) or 5 mL serological pipettes plugged with a small piece of Pyrex glass wool in the tip. (Pyrex glass wool shall be pre-rinsed with appropriate solvents to ensure its cleanliness.) The Kontes column may be plugged with Pyrex glass wool or a polyethylene porous disk (Kontes K-420162).

3.2.3.15 Pyrex glass wool.

3.2.3.16 Bottle or test tube, 50 mL with Teflon-lined screw cap for sulfur removal.

3.2.3.17 Pasteur pipettes, disposable.

3.2.4 Reagents

3.2.4.1 Sodium Sulfate, anhydrous <u>powdered</u> reagent grade, heated at 400°C for four hours, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog #73898 or equivalent.

3.2.4.2 Methylene chloride, hexane, acetone, isooctane, 2-propanol and benzene - pesticide quality or equivalent.

3.2.4.3 Alumina - neutral, Super I Woelm (Universal Scientific, Atlanta, GA) or equivalent. Prepare activity III by adding 7% (v/w) reagent water to the Super I neutral alumina. Tumble or shake on a wrist action shaker for a minimum of two hours or preferably overnight. There

should be no lumps present. Store in a tightly sealed glass container. A 25 cycle soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide techniques indicate any interferences for the compounds of interest.

3.2.4.3.1 Alumina Equivalency Check. Test the alumina by adding the BNA surrogates (see method PNL-ALO-344) in 1:1 acetone/hexane to the alumina and following paragraph 3.2.8.1. The tribromophenol should not be detected by GC/EC if the alumina and its activation are acceptable. Also check recovery of all single component pesticides following the same procedure. The percent recovery for all single component pesticides must be ≥80%, except for endosulfan sulfate which must be ≥60% and endrin aldehyde which is not recovered. The data must be retained by the Contractor and made available for inspection during on-site evaluations. If the alumina deactivated with 7% (v/w) reagent water does not prove adequate to remove the BNA surrogates and other interferences, the alumina may be deactivated with as much as 9% reagent water, so long as the criteria for tribromophenol and the recovery of all single component pesticides can be met.

3.2.4.4 Reagent water - Reagent water is defined as water in which an interferant is not observed at or above the CRQL of each parameter of interest.

3.2.4.5 TBA - sulfite reagent. Dissolve 3.39 g TBA hydrogen sulfate in 100 mL distilled water. To remove impurities, extract this solution three times with 20 mL portions of hexane. Discard the hexane extracts and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw cap. This solution can be stored at room temperature for at least one month.

3.2.4.6 GPC calibration solutions:

3.2.4.6.1 Corn oil - 200 mg/mL in methylene chloride.

3.2.4.6.2 Bis(2-ethylhexylphthalate) and pentachlorophenol - 4.0 mg/mL in methylene chloride.

3.2.4.7 Sodium Sulfite, reagent grade.

3.2.4.8 Surrogate standard spiking solution.

3.2.4.8.1 Pesticide surrogate standard spiking solution.

3.2.4.8.1.1 The surrogate standard is added to all samples, blanks, matrix spike, matrix spike duplicates and calibrations solution; the compound specified for this purpose is dibutylchlorendate.

3.2.4.8.1.2 Prepare a surrogate standard spiking solution at a concentration of 20 µg/1.0 mL in methanol. Store the spiking solutions at 4°C (±2°C) Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner if comparison with quality control check samples indicates a problem.

3.2.4.9 Matrix standard spiking solutions.

3.2.4.9.1 Pesticide matrix standard spiking solution. Prepare a spiking solution in methanol that contains the following pesticides in the concentrations specified below. Store spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner if comparison with quality control check samples indicate a problem.

PESTICIDE	µg/1.0 mL
Lindane	2.0
Heptachlor	2.0
Aldrin	2.0
Dieldrin	5.0
Endrin	5.0
4,4' DDT	5.0

Matrix spikes are also to serve as duplicates, therefore, add volume specified in Sample Extraction section to each of two 30 g portions from one sample chosen for spiking.

3.2.5 Sample Extraction

3.2.5.1 Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves and rocks.

3.2.5.1.1 Transfer 50 g of soil/sediment to 100 mL beaker. Add 50 mL of water and stir for one hour. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the cognizant scientist for instructions on how to handle the sample. Discard this portion of sample.

NOTE: Recovery of dibutylchlorendate will be low if pH is outside this range.

3.2.5.2 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample to the nearest 0.1 g into a 200 mL centrifuge bottle and add 60 g of anhydrous powdered sodium sulfate. Mix well. The sample should have a sandy texture at this point. Immediately, add 100 mL of 1:1 methylene chloride - acetone to the sample.

3.2.5.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

3.2.5.2.2 Weigh out two 30 g (record weight to nearest 0.1 g) portions for use as matrix and matrix spike duplicates. Follow paragraph 3.2.5.2. When using GPC cleanup, add 800 µL of the pesticide matrix spike to each of the other two portions. When <u>not</u> using GPC cleanup, add 400 µL of the pesticide matrix spike to each of the two portions.

3.2.5.2.3 When using GPC, add 200 µL of pesticide surrogate to the sample. When <u>not</u> using GPC, add 100 µL of pesticide surrogate to the sample.

3.2.5.3 Place the bottom surface of the tip of the 3/4 in. disrupter horn about 1/2 in. below the surface of the solvent but above the sediment layer.

3.2.5.4 Sonicate for 1 1/2 minutes with the W-385 (or 3 minutes with the W-375), using No. 208 3/4 in. standard disrupter

horn with output control knob set at 10 (or No. 305 3/4 in. tapped high gain "Q" disrupter horn at 5) and mode switch on "1 sec. pulse" and % duty cycle knob set at 50%. Do NOT use MICROTIP probe.

3.2.5.5 Decant and filter extracts through Whatman #41 filter paper using vacuum or gravity filtration or centrifuge and decant extraction solvent.

3.2.5.6 Repeat the extraction two more times with two additional 100 mL portions of 1:1 methylene chloride - acetone. Before each extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or very carefully with the tip of the unenergized probe. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the funnel and rinse with 1:1 methylene chloride - acetone.

3.2.5.7 Transfer the extract to a K-D concentrator consisting of a 10 mL concentrator tube and a 500 mL evaporative flask. Other concentration devices or techniques may be used if equivalency is demonstrated for all extractable and pesticide compounds listed in method PNL-ALO-346.

3.2.5.8 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding an apparent volume of 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 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 15 minutes. A longer period of time for the concentration may be required if the temperature is maintained 90°C or less if the concentration process is performed in a high air flow radiochemistry hood. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes, and make up to 10 mL volume with methylene chloride.

3.2.5.9 If GPC cleanup is not used proceed to paragraph 3.2.7.

3.2.6 Extract Cleanup

3.2.6.1 GPC Set-up and Calibration

3.2.6.1.1 Packing the column - Place 70 g of Bio Beads SX-3 in a 400 mL beaker. Cover the beads with methylene chloride; allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to top, at 5.0 mL/minute. After approximately one hour, adjust the pressure on the column to 7 to 10 psi and pump an additional four hours to remove air from the column. Adjust the column pressure periodically as required to maintain 7 to 10 psi.

3.2.6.1.2 Calibration of the column - Load 5 mL of the corn oil solution into sample loop No. 1 and 5 mL of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10 mL fraction (i.e., change fraction at two minute intervals) for 36 minutes. Inject the phthalate-phenol solution and collection 15 mL fractions for 60 minutes. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID on the DB-5 capillary column, a UV spectrophotometer or a GC/MS system. Plot the concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose a "dump time" which allows ≥85% removal of the corn oil and ≥85% recovery of the bis(2-ethylhexyl)-phthalate. Choose the "collect time" to extend at least 10 minutes after the elution of pentachlorophenol. Wash the column at least 15 minutes between sample. Typical parameters selected are: Dump time, 30 minutes (150 mL), collect time, 36 minutes (180 mL), and wash time, 15 minutes (75 mL). The column can also be calibrated by the use of a 254 mm UV detector in place of gravimetric and GC analyses of fractions. Measure the peak areas at various elution times to determine appropriate fractions.

The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. System calibration usually remains constant over this period of time if column flow rate remains constant.

3.2.6.2 GPC Extract Cleanup

Prefilter or load all extracts via the filter holder to avoid particulates that might stop the flow. Load one 5.0 mL aliquot of the extract onto the GPC column. Do not apply excessive pressure when loading the GPC. Purge the sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carry-over. Process the extracts using the dump, collect and wash parameters determined from the calibration and collect the cleaned extracts in 400 mL beakers tightly covered with aluminum foil. The phthalate-phenol calibration solution shall be taken through the cleanup cycle with each set of 23 extracts loaded into the GPC. The recovery for each compound must be ≥85%. This must be determined on a GC/FID, using a DB-5 capillary column, a UV recording spectrophotometer or a GC/MS system. A copy of the printouts of standard and check solution are required as deliverables with each case. Show % recovery on the copy.

3.2.6.2.1 If GPC cleanup of samples is required because of poor GC/EC chromatography in method PNL-ALO-346 dilute the extract to 10 mL with methylene chloride and perform GPC cleanup as per paragraph 3.2.6.2. The reagent blank accompanying the samples should be included, unless only one or a partial group of samples requires cleanup. In this case, set up a new reagent blank with 10 mL of methylene chloride and appropriate surrogate standard added.

3.2.6.3 Concentrate the extract as per paragraphs 3.2.5.7 and 3.2.5.8.

3.2.7 Final Concentration of Extract with Optional Extract Splitting Procedure

If the extract in paragraph 3.2.5.8 is to be used only for pesticide/PCB analysis, it must be concentrated to a volume of 1.0 mL, following the procedure in paragraph 3.2.7.1.

If the extract in paragraph 3.2.5.8 is to be used for <u>both</u> semi-volatile and pesticide/PCB analyses, then it must be split into two portions. In that case, follow the procedure in paragraph 3.2.7.1 to obtain the pesticides portion, and follow that with the procedure in paragraph 3.2.7.2 to obtain the semi-volatile portion.

Refer to method PNL-ALO-344 for specific instructions regarding the treatment of extracts for semi-volatile analysis.

3.2.7.1 If the extract is to be used only for the pesticide/PCB analysis, or if the same extract is used for both semi-volatile and pesticide/PCB analyses, to split out the pesticide/PCB extract, transfer 0.5 mL of the 10 mL methylene chloride extract to a separate concentrator tube. Add 5 mL of hexane and a silicon carbide boiling chip and mix using vortex mixer, or if added in this order, allow mixing to occur with boiling. Attach a two-ball micro-Snyder column. Pre-wet the Snyder column by adding 0.5 mL of hexane 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. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. A longer period of time for the concentration may be required if the temperature is maintained 90°C or less and if the concentration process is performed in a high air flow radiochemistry hood. Concentrate the extract to an apparent volume of less than 1 mL. Use Nitrogen blowdown (see paragraph 3.2.7.3) or the micro-Snyder column technique (see Section 2.2.7.2 of method PNL-ALO-344) to reduce the volume to 0.5 mL. Add 0.5 mL of acetone. The pesticide extract must now be passed through an alumina column to remove the BNA surrogates and polar interferences. Proceed to paragraph 3.2.8.

3.2.7.2 If the extract in paragraph 3.2.5.8 <u>was</u> split in paragraph 3.2.7.1 to obtain a portion for pesticides analysis, the portion for semi-volatile analysis must be treated according to the procedures in method PNL-ALO-344 section 3.2.7.2.2.

3.2.7.3 Nitrogen blowdown technique (taken from ASTM Method D 3086). Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to below 1 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). **CAUTION:** New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

The internal wall of the tube must be rinsed down several times with hexane during the operation. During

evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry. If GPC cleanup techniques were employed, the 0.5 mL volume represents a two-fold dilution to account for the fact that only half the extract went through the GPC, and therefore, the sample detection limit would be 2x CRQL see page 6 of method PNL-ALO-346.

3.2.7.4 Store all extracts at 4°C (±2°C) in the dark in Teflon-sealed containers until all analyses are performed.

3.2.8 Pesticide/PCB

3.2.8.1 Alumina Column Cleanup

All samples prepared from the same extract as used for the semi-volatile analysis must be taken through this cleanup technique to eliminate BNA surrogates that will interfere in the GC/EC analysis.

3.2.8.1.1 Add 3 g of activity III neutral alumina to the 10 mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

3.2.8.1.2 Transfer the 1.0 mL of hexane/acetone extract from paragraph 3.2.7.1 to the top of the alumina using a disposable Pasteur pipette. Collect the eluate in a clean, 10 mL concentrator tube.

3.2.8.1.3 Add an apparent volume of 1 mL of hexane to the original extract concentrator tube to rinse it. Transfer these rinsings to the alumina column. Elute the column with an additional 9 mL of hexane. Do not allow the column to go dry during the addition and elution of the sample.

3.2.8.1.4 Concentrate the extract to 1.0 mL following either paragraph 3.2.7.1 or 3.2.7.3, using hexane where methylene chloride is specified. When concentrating medium level extracts, the Nitrogen blowdown technique can be used to avoid contaminating the micro-Snyder column.

3.2.8.2 Observe the appearance of the extract.

3.2.8.2.1 If crystals of sulfur are evident or sulfur is expected to be present, proceed to paragraph 3.2.8.3.

3.2.8.2.2 If the sulfur is not expected to be a problem, transfer the 1.0 mL to a GC vial and label as Pesticide/PCB fraction. The extract is ready for GC/EC analysis. Store the extracts at 4°C (±2°C) in the dark until analyses are performed.

3.2.8.3 Optional Sulfur Cleanup

3.2.8.3.1 Transfer the 1.0 mL from paragraph 3.2.8.2 to a 50 mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1.0 mL of hexane, adding the rinsings to the 50 mL bottle. If only a partial set of samples requires sulfur cleanup, set up a new reagent blank with 1.0 mL of hexane and take it through the sulfur cleanup. Include the surrogate standards.

3.2.8.3.2 Add 1 mL TBA-sulfite reagent and 1 mL 2-propanol, cap the bottle, and shake for at least 1 minute. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100 mg portions until a solid residue remains after repeated shaking.

3.2.8.3.3 Add 5 mL distilled water and shake for at least one minute. Allow the sample to stand for 5 - 10 minutes and remove the hexane layer (top) for analysis. Concentrate the hexane to 1.0 mL as per paragraphs 3.2.7.1 and 3.2.7.3 using hexane where methylene chloride is specified. The temperature for the water bath should be about 80°C for the micro Snyder column technique. Continue as outlined in paragraph 3.2.8.2.2.

4.0 Records

Records shall be maintained and controlled so as to conform to requirements of the ACL Quality Assurance Plan, MCS-033. Bench Sheets and/or Laboratory Record Book provide a mechanism for control of records generated in performance of this procedure.

5.0 Specific Qualifications

None required, although NIST-traceable surrogate and matrix spike standards are used as part of the QA protocol, and are measured in the self-qualifying procedure PNL-ALO-346.

REFERENCES

USEPA Contract Laboratory Program Statement Of Work For Organic Analysis, Multi-Media, Multi-Concentration, 2/88, pages D-7/PEST through D-30/PEST and Exhibit A.

PNL-ALO-346, Analysis for Pesticides/PCBs by Gas Chromatography with Electron Capture Detection. PNL-MA-599.

PNL-ALO-120, Procedure for Extraction of Single Shell Tank Samples for the Analysis of Semi-Volatile Organic Compounds. PNL-MA-599.

PNL-ALO-344, Procedure for Sample Preparation of Samples for GC/MS Analysis for Semi-Volatile Organic Compounds. PNL-MA-599.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-350, REPORT PREPARATION

APPLICABILITY

This procedure describes the preparation of reports for the organic analysis. The procedure includes preparation of both the report and the deliverables packages according to the USEPA Contract Laboratory Program Statement of Work (CLP SOW). However, there is no intent to specify the deliverables content. The deliverables will be dependent on the program Statement of Work. The package can be simple containing just analytical results, or it could also include raw data and QA/QC information, or it could contain all components required by the CLP SOW which is a very extensive package.

DEFINITIONS

None

RESPONSIBLE STAFF

Cognizant Scientist

PROCEDURE

See Attachment 1 for the detailed procedure.

QUALITY CONTROL

None

REFERENCES

USEPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, 2/88, B-6 through B-42 and Section IV of Exhibit B.

Author	Date	Project Mgr.	Date	QAD Representative	Date
[signature]	7/28/89			S L English	7-28-89
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
[signature]	7-28-89	[signature]	7/28/89		

Procedure No.	Revision No.	Effective Date	Page	of
PNL-ALO-350	0	AUG 03 1989	1	1

SECTION II

REPORT DESCRIPTIONS AND ORDER OF DATA DELIVERABLES

The Contractor laboratory shall provide reports and other deliverables as specified in the Contract Schedule (Performance/Delivery Schedule, Section F.1). The required content and form of each deliverable is described in this Exhibit.

All reports and documentation MUST BE:

- Legible,
- Clearly labeled and completed in accordance with instructions in this Exhibit,
- Arranged in the order specified in this Section, and
- Paginated.

If submitted documentation does not conform to the above criteria, the Contractor will be required to resubmit such documentation with deficiency(ies) corrected, at no additional cost to the Agency.

Whenever the Contractor is required to submit or resubmit data as a result of an on-site laboratory evaluation or through a PO/DPO action, the data must be clearly marked as ADDITIONAL DATA and must be sent to all three contractual data recipients (SMO, EMSL-LV, and Region). A cover letter shall be included which describes what data is being delivered, to which EPA Case(s) it pertains, and who requested the data.

Whenever the Contractor is required to submit or resubmit data as a result of Contract Compliance Screening (CCS) review by SMO, the data must be sent to all three contractual data recipients (SMO, EMSL/LV and Region), and in all three instances must be accompanied by a color-coded COVER SHEET (Laboratory Response To Results of Contract Compliance Screening) provided by SMO.

Section III of this Exhibit contains copies of the required data reporting forms in Agency-specified formats, along with instructions to assist the Contractor in accurately providing the Agency all required data. Data elements with field parameters for reporting data in computer readable form are contained in Exhibit H.

Descriptions of the requirements for each deliverable item cited in the Contract Performance/Delivery Schedule (Contract Schedule, Section F.1) are specified in parts A-G of this Section. Items submitted concurrently MUST BE arranged in the order listed. Additionally, the components of each item MUST BE arranged in the order presented in this Section when the item is submitted.

Examples of specific data deliverables not included herein may be obtained by submitting a written request to the EPA Project Officer, stating the information requested, and signed by the Laboratory Manager.

A. Contract Start-Up Plan

The Contractor shall submit a contract start-up plan for EPA approval as specified in the Contract Performance/Delivery Schedule. The plan shall set forth the Contractor's proposed schedule for receiving samples starting with the 30th calendar day after award and ending with the date the Contractor is capable of receiving the full monthly sample allotment stipulated in the Contract. The Project Officer will review the contract start-up plan within 7 days of submission and will notify the Contractor of the plan's status.

NOTE: The Contractor shall be required to receive samples within 30 days of contract award. EPA can't guarantee exact adherence to start-up plan that is agreed upon by the PO and Contractor, but will attempt to meet it as close as possible.

B. Updated SOPs

The Contractor shall submit updated copies of all required Standard Operating Procedures (SOPs) that were submitted with the prebid Performance Evaluation sample results. The updated SOPs must address any and all issues of laboratory performance and operation identified through the review of the Performanc Evaluation sample data and the evaluation of Bidder-Supplied Documentation.

The Contractor must supply SOPs for:

1. Sample receipt and logging.
2. Sample and extract storage.
3. Preventing sample contamination.
4. Security for laboratory and samples.
5. Traceability/Equivalency of standards.
6. Maintaining instrument records and logbooks.
7. Sample analysis and data control systems.
8. Glassware cleaning.
9. Technical and managerial review of laboratory operation and data package preparation.
10. Internal review of contractually-required quality assurance and quality control data for each individual data package.
11. Sample analysis, data handling and reporting.
12. Chain-of-custody.
13. Document control, including case file preparation.

Note: Such documentation is not required to conform specifically (i.e., in every detail) to this contract's requirements, but shall be representative of standard laboratory operations, and shall give clear evidence of the Contractor's ability to successfully fulfill all contract requirements.

C. Sample Traffic Reports

Original Sample Traffic Report page marked "Lab Copy for Return to SMO" with lab receipt information and signed in original Contractor signature, for each sample in the Sample Delivery Group.

Traffic Reports (TRs) shall be submitted in Sample Delivery Group (SDG) sets (i.e., TRs for all samples in an SDG shall be clipped together), with an SDG Cover Sheet attached.

The SDG Cover Sheet shall contain the following items:

- Lab name
- Contract number
- Sample Analysis Price - full sample price from contract.
- Case Number
- List of EPA sample numbers of all samples in the SDG, identifying the first and last samples received, and their dates of receipt (LRDs). NOTE: When more than one sample is received in the first or last SDG shipment, the "first" sample received would be the lowest sample number (considering both alpha and numeric designations); the "last" sample received would be the highest sample number (considering both alpha and numeric designations).

In addition, each Traffic Report must be clearly marked with the SDG Number, the sample number of the first sample in the SDG (as described in the following paragraph). This information should be entered below the Lab Receipt Date on the TR. In addition, the TR for the last sample received in the SDG must be clearly marked "SDG - FINAL SAMPLE."

The EPA sample number of the first sample received in the SDG is the SDG number. When several samples are received together in the first SDG shipment, the SDG number shall be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG. (The SDG number is also reported on all data reporting forms. See Section III, Forms Instruction Guide.)

If samples are received at the laboratory with multi-sample Traffic Reports (TRs), all the samples on one multi-sample TR may not necessarily be in the same SDG. In this instance, the laboratory must make the appropriate number of photocopies of the TR, and submit one copy with each SDG cover sheet.

D. Sample Data Summary Package

As specified in the Delivery Schedule, one Sample Data Summary Package shall be delivered to SMO concurrently with delivery of other required sample data. The Sample Data Summary Package consists of copies of specified items from the Sample Data Package. These items are listed below and described under part E, Sample Data Package.

The Sample Data Summary Package shall be ordered as follows and shall be submitted separately (i.e., separated by rubber bands, clips or other means) directly preceding the Sample Data Package. Sample data forms shall be arranged in increasing EPA sample number order, considering both letters and numbers. BE400 is a lower sample number than BF100, as E precedes F in the alphabet.

The Sample Data Summary Package shall contain data for samples in one Sample Delivery Group of the Case, as follows:

1. Case Narrative

2. By fraction (VOA, SV, PEST) and by sample within each fraction - tabulated target compound results (Form I) and tentatively identified compounds (Form I, TIC)(VOA and SV only)

3. By fraction (VOA, SV, PEST) - surrogate spike analysis results (Form II) by matrix (water and/or soil) and for soil, by concentration (low or medium)

4. By fraction (VOA, SV, PEST) - matrix spike/matrix spike duplicate results (Form III)

5. By fraction (VOA, SV, PEST) - blank data (Form IV) and tabulated results (Form I) including tentatively identified compounds (Form I, TIC)(VOA and SV only).

6. By fraction (VOA, SV only) - internal standard area data (Form VIII).

E. Sample Data Package

The Sample Data Package is divided into the five major units described below. The last three units are each specific to an analytical fraction (volatiles, semivolatiles, pesticides/PCBs). If the analysis of a fraction is not required, then that fraction-specific unit is not required as a deliverable.

The Sample Data Package shall include data for analyses of all samples in one Sample Delivery Group, including field samples, reanalyses, blanks, matrix spikes, and matrix spike duplicates.

1. Case Narrative

This document shall be clearly labeled "Case Narrative" and shall contain: laboratory name; Case number; sample numbers in the Sample Delivery Group (SDG), differentiating between initial analyses and re-analyses; SDG number; Contract number; and detailed documentation of any quality control, sample, shipment and/or analytical problems encountered in processing the samples reported in the data package.

Whenever data from sample re-analyses are submitted, the Contractor shall state in the Case Narrative for each re-analysis, whether it considers the re-analysis to be billable, and if so, why.

The Contractor must also include any problems encountered; both technical and administrative, the corrective actions taken, and resolution.

The Case Narrative shall contain the following statement, verbatim: "I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package and in the computer-readable data submitted on floppy diskette has been authorized by the Laboratory Manager or his designee, as verified by the following signature." This statement shall be directly followed by signature of the Laboratory Manager or his designee with a typed line below it containing the signer's name and title, and the date of signature.

Additionally, the Case Narrative itself must be signed in original signature by the Laboratory Manager or his designee and dated.

2. Traffic Reports

A copy of the Sample Traffic Reports submitted in Item A for all of the samples in the SDG. The Traffic Reports shall be arranged in increasing EPA sample number order, considering both letters and numbering in ordering samples.

If samples are received at the laboratory with multi-sample Traffic Reports (TRs), all the samples on one multi-sample TR may not necessarily be in the same SDG. In this instance, the laboratory must make the appropriate number of photocopies of the TR so that a copy is submitted with each data package to which it applies. In addition, in any instance where samples from more than one multi-sample TR are in the same data package, the laboratory must submit a copy of the SDG cover sheet with copies of the TRs.

3. Volatiles Data

a. QC Summary

(1) Surrogate Percent Recovery Summary (Form II VOA)

(2) Matrix Spike/Matrix Spike Duplicate Summary (Form III VOA)

(3) Method Blank Summary (Form IV VOA)

(If more than a single form is necessary, forms must be arranged in chronological order by date of analysis of the blank.)

(4) GC/MS Tuning and Mass Calibration (Form V VOA)

BFB in chronological order; by instrument.

(5) Internal Standard Area Summary (Form VIII VOA)

In chronological order; by instrument.

b. Sample Data

Sample data shall be arranged in packets with the Organic Analysis Data Sheet (Form I VOA, including Form I VOA-TIC), followed by the raw data for volatile samples. These sample packets should then be placed in increasing EPA sample number order, considering both letters and numbers in ordering samples.

(1) TCL Results - Organic Analysis Data Sheet (Form I VOA).

Tabulated results (identification and quantitation) of the specified target compounds (Exhibit C). The validation and release of these results is authorized by a specific, signed statement in the Case Narrative (reference C.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the Case Narrative.

On Form I, the appropriate concentration units shall be entered. For example, ug/L for water samples or ug/Kg for soil/sediment samples. No other units are acceptable. NOTE: Report analytical results to one significant figure if the value is less than 10; to two significant figures above 10.

(2) Tentatively Identified Compounds (Form I VOA-TIC).

This form must be included even if no compounds are found. If so, indicate this on the form by entering "0" in the field for "Number found."

Form I VOA-TIC is the tabulated list of the highest probable match for up to 10 of the nonsurrogate organic compounds not listed in Exhibit C (TCL), including the CAS (Chemical Abstracts Registry) number, tentative identification and estimated concentration. For estimating concentration, assume a response factor of 1, and estimate the concentration by comparison of the compound peak height or total area count to the peak height or total area count of the nearest internal standard free of interferences on the reconstructed ion chromatogram. NOTE: The laboratory must be consistent (i.e., use peak height for all comparisons or use total area count for all comparisons).

(3) Reconstructed total ion chromatograms (RIC) for each sample or sample extract.

RICs must be normalized to the largest nonsolvent component, and must contain the following header information:

- EPA sample number
- Date and time of analysis
- GC/MS instrument ID
- Lab file ID

Internal standard and surrogate spiking compounds are to be labeled with the names of compounds, either directly out from the peak, or on a print-out of retention times if retention times are printed over the peak. If automated data system procedures are used for preliminary identification and/or quantification of the Target Compound List (TCL) compounds, the complete data system report must be included in all sample data packages, in addition to the reconstructed ion chromatogram. The complete data system report shall include all of the information listed below. For laboratories which do not use the automated data system procedures, a laboratory "raw data sheet," containing the following information, must be included in the sample data package in addition to the chromatogram.

- EPA sample number
- Date and time of analysis
- RT or scan number of identified TCL compounds
- Ion used for quantitation with measured area
- Copy of area table from data system
- GC/MS instrument ID
- Lab file ID

(4) For each sample, by each compound identified:

(a) Copies of raw spectra and copies of background-subtracted mass spectra of target compounds listed in Exhibit C (TCL) that are identified in the sample and corresponding background-subtracted TCL standard mass spectra. Spectra must be labeled with EPA sample number, lab file ID, date and time of analysis, and GC/MS instrument ID; compound names must be clearly marked on all spectra.

(b) Copies of mass spectra of nonsurrogate organic compounds not listed in Exhibit C (TCL) (Tentatively Identified Compounds) with associated best-match spectra (three best matches), labeled as in (4)(a) above.

c. Standards Data

(1) Initial Calibration Data (Form VI VOA) - in order by instrument, if more than one instrument used.

(a) VOA standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for the initial (five point) calibration, labeled as in b.(3) above. Spectra are not required.

(b) All initial calibration data must be included, regardless of when it was performed and for which case. When more than one initial calibration is performed, the data must be put in chronological order, by instrument.

(2) Continuing Calibration (Form VII VOA) - in order by instrument, if more than one instrument used.

(a) VOA standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for all continuing (12 hour) calibrations, labeled as in b.(3) above. Spectra are not required.

(b) When more than one continuing calibration is performed, forms must be in chronological order, within fraction and instrument.

(3) Internal Standard Area Summary (Form VIII VOA) - in order by instrument, if more than one instrument used.

When more than one continuing calibration is performed, forms must be in chronological order, by instrument.

d. Raw QC Data

(1) BFB (for each 12-hour period, for each GC/MS system utilized)

(a) Bar graph spectrum, labeled as in b.(3) above.

(b) Mass listing, labeled as in b.(3) above.

(2) Blank Data - in chronological order. NOTE: This order is different from that used for samples.

(a) Tabulated results (Form I VOA)

(b) Tentatively Identified Compounds (Form I VOA-TIC) even if none found.

(c) Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in b.(3) above.

(d) TCL spectra with lab generated standard, labeled as in b.(4) above. Data systems which are incapable of dual display shall provide spectra in order:

- o Raw TCL compound spectra
- o Enhanced or background subtracted spectra
- o Laboratory generated TCL standard spectra

(e) GC/MS library search spectra for Tentatively Identified Compounds (TIC), labeled as in b.(4) above.

(f) Quantitation/Calculation of Tentatively Identified Compound(s) (TIC) concentrations

(3) Matrix Spike Data

(a) Tabulated results (Form I VOA) of nonspiked TCL compounds. Form I VOA-TIC not required.

(b) Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in b.(4) above. Spectra not required.

(4) Matrix Spike Duplicate Data

(a) Tabulated results (Form I VOA) of nonspiked TCL compounds. Form I VOA-TIC not required.

(b) Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in b.(4) above. Spectra not required.

4. Semivolatiles Data

a. QC Summary

(1) Surrogate Percent Recovery Summary (Form II SV)

(2) Matrix Spike/Matrix Spike Duplicate Summary (Form III SV)

(3) Method Blank Summary (Form IV SV)

(If more than a single form is necessary, forms must be arranged in chronological order by date of analysis of the blank.)

(4) GC/MS Tuning and Mass Calibration (Form V SV)

DFTPP in chronological order; by instrument.

(5) Internal Standard Area Summary (Form VIII SV)

In chronological order; by instrument.

b. Sample Data

Sample data shall be arranged in packets with the Organic Analysis Data Sheet (Form I SV, including Form I SV-TIC), followed by the raw data for semivolatile samples. These sample packets should then be placed in increasing EPA sample number order, considering both letters and numbers in ordering samples.

(1) TCL Results - Organic Analysis Data Sheet (Form I SV-1, SV-2).

Tabulated results (identification and quantitation) of the specified target compounds (Exhibit C). The validation and release of these results is authorized by a specific, signed statement in the Case Narrative (reference E.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the Case Narrative.

On Form I, the appropriate concentration units shall be entered. For example, ug/L for water samples or ug/Kg for soil/sediment samples. No other units are acceptable. NOTE: Report analytical results to one significant figure if the value is less than 10; to two significant figures above 10.

(2) Tentatively Identified Compounds (Form I SV-TIC).

This form must be included even if no compounds are found. If so, indicate this on the form by entering "0" in the field for "Number found".

Form I SV-TIC is the tabulated list of the highest probable match for up to 20 of the nonsurrogate organic compounds not listed in Exhibit C (TCL), including the CAS (Chemical Abstracts Registry) number, tentative identification and estimated concentration. For estimating concentration, assume a response factor of 1, and estimate the concentration by comparison of the compound peak height or total area count to the peak height or total area count of the nearest internal standard free of interferences on the reconstructed ion chromatogram. NOTE: The laboratory must be consistent (i.e., use peak height for all comparisons or use total area count for all comparisons).

(3) Reconstructed total ion chromatograms (RIC) for each sample, sample extract, standard, blank, and spiked sample.

RICs must be normalized to the largest nonsolvent component, and must contain the following header information:

- o EPA sample number
- o Date and time of analysis
- o GC/MS instrument ID
- o Lab file ID

Internal standard and surrogate spiking compounds are to be labeled with the names of compounds, either directly out from the peak, or on a print-out of retention times if retention times are printed over the peak. If automated data system procedures are used for preliminary identification and/or quantification of the Target Compound List (TCL) compounds, the complete data system report must be included in all sample data packages, in addition to the reconstructed ion chromatogram. The complete data system report shall include all of the information listed below. For laboratories which do not use the automated data system procedures, a laboratory "raw data sheet," containing the following information, must be included in the sample data package in addition to the chromatogram.

- o EPA sample number
- o Date and time of analysis
- o RT or scan number of identified TCL compounds
- o Ion used for quantitation with measured area
- o Copy of area table from data system
- o GC/MS instrument ID
- o Lab file ID

(4) For each sample, by each compound identified:

(a) Copies of raw spectra and copies of background-subtracted mass spectra of target compounds listed in Exhibit C (TCL) that are identified in the sample and corresponding background-subtracted TCL standard mass spectra. Spectra must be labeled with EPA sample number, lab file ID, date and time of analysis, and GC/MS instrument ID; compound names must be clearly marked on all spectra.

(b) Copies of mass spectra of nonsurrogate organic compounds not listed in Exhibit C (TCL) (Tentatively Identified Compounds) with associated best-match spectra (three best matches), labeled as in (4)(a) above.

(c) GPC chromatograms (if GPC performed).

c. Standards Data

(1) Initial Calibration Data (Form VI SV-1, SV-2) - in order by instrument, if more than one instrument used.

(a) BNA standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for the initial (five point) calibration, labeled as in b.(3) above. Spectra are not required.

(b) All initial calibration data must be included, regardless of when it was performed and for which case. When more than one initial calibration is performed, the data must be put in chronological order, by instrument.

(2) Continuing Calibration (Form VII SV-1, SV-2) - in order by instrument, if more than one instrument used.

(a) BNA standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for all continuing (12 hour) calibrations, labeled as in b.(3) above. Spectra are not required.

(b) When more than one continuing calibration is performed, forms must be in chronological order, by instrument.

(3) Internal Standard Area Summary (Form VIII SV-1, SV-2) - in order by instrument, if more than one instrument used.

When more than one continuing calibration is performed, forms must be in chronological order by instrument.

d. Raw QC Data

(1) DFTPP (for each 12-hour period, for each GC/MS system utilized)

(a) Bar graph spectrum, labeled as in b.(3) above.

(b) Mass listing, labeled as in b.(3) above.

(2) Blank Data - in chronological order. NOTE: This order is different from that used for samples.

(a) Tabulated results (Form I SV-1, SV-2)

(b) Tentatively Identified Compounds (Form I SV-TIC) - even if none found.

(c) Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in b.(3) above.

(d) TCL spectra with lab generated standard, labeled as in b.(4) above. Data systems which are incapable of dual display shall provide spectra in order:

- o Raw TCL compound spectra
- o Enhanced or background subtracted spectra
- o Laboratory generated TCL standard spectra

(e) GC/MS library search spectra for Tentatively Identified Compounds (TIC), labeled as in b.(4) above.

(f) Quantitation/Calculation of Tentatively Identified Compound(s) (TIC) concentrations

(3) Matrix Spike Data

(a) Tabulated results (Form I) of nonspiked TCL compounds. Form 1 SV-TIC not required.

(b) Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in b.(3) above. Spectra not required.

(4) Matrix Spike Duplicate Data

(a) Tabulated results (Form I SV-1, SV-2) of nonspiked TCL compounds. Form 1 SV-TIC not required.

(b) Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in b.(3) above. Spectra not required.

5. Pesticide/PCB Data

a. QC Summary

(1) Surrogate Percent Recovery Summary (Form II PEST)

(2) Matrix Spike/Matrix Spike Duplicate Summary (Form III PEST)

(3) Method Blank Summary (Form IV PEST)

(If more than a single form is necessary, forms must be arranged in chronological order by date of analysis of the blank.)

b. Sample Data

Sample data shall be arranged in packets with the Organic Analysis Data Sheet (Form I PEST), followed by the raw data for pesticide samples. These sample packets should then be placed in increasing EPA sample number order, considering both letters and numbers in ordering samples.

(1) TCL Results - Organic Analysis Data Sheet (Form I PEST).

Tabulated results (identification and quantitation) of the specified target compounds (Exhibit C). The validation and release of these results is authorized by a specific, signed statement in the Case Narrative (reference E.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the Case Narrative.

On Form I PEST, the appropriate concentration units shall be entered. For example, ug/L for water samples or ug/Kg for soil/sediment samples. No other units are acceptable.

NOTE: Report analytical results to two significant figures for all pesticide/PCB samples.

(2) Copies of pesticide chromatograms.

All chromatograms must be labeled with the following information:

- o EPA sample number
- o Volume injected (ul)
- o Date and time of injection
- o GC column identification (by stationary phase)
- o GC instrument identification
- o Positively identified compounds must be labeled with the names of compounds, either directly out from the peak, or on a print-out of retention times if retention times are printed over the peak.

(3) Copies of pesticide chromatograms from second GC column confirmation. Chromatograms to be labeled as in (2) above.

(4) GC Integration report or data system printout and calibration plots (area vs. concentration) for 4,4'-DDT, 4,4'-DDD, 4,4'-DDE or toxaphene (where appropriate).

(5) Manual work sheets.

(6) UV traces from GPC (if available).

(7) If pesticide/PCBs are confirmed by GC/MS, the Contractor shall submit copies of raw spectra and copies of background-subtracted mass spectra of target compounds listed in Exhibit C (TCL) that are identified in the sample and corresponding background-subtracted TCL standard mass spectra. Compound names must be clearly marked on all spectra. For multicomponent pesticides/PCBs confirmed by GC/MS, the Contractor shall submit mass spectra of 3 major peaks of multicomponent compounds from samples and standards.

c. Standards Data

(1) Form VIII PEST - Pesticide Evaluation Standards Summary (all GC columns)

(2) Form IX PEST - Pesticide/PCB Standards Summary (all GC columns)

(3) Form X PEST - Pesticide/PCB Identification (only required for positive results)

(4) Pesticide standard chromatograms and data system printouts for <u>all</u> standards to include:

- o Evaluation Standard Mix A
- o Evaluation Standard Mix B
- o Evaluation Standard Mix C
- o Individual Standard Mix A
- o Individual Standard Mix B
- o All multiresponse pesticides/PCBs
- o All quantitation standards
- o A copy of the computer reproduction or strip chart recorder output covering the 100 fold range

(a) All chromatograms are required to have the following:

- o Label all chromatograms with the "EPA Sample Number" for standards, i.e. EVALA, EVALB, etc. (See Forms Instructions for details).

- Label all standard peaks for all individual compounds either directly out from the peak or on the printout of retention times if retention times are printed over the peak.
- List total ng injected for each standard.
- A printout of retention times and corresponding peak areas must accompany each chromatogram.
- Date and time of injection.
- GC column identification (by stationary phase).
- GC instrument identification.

d. Raw QC Data

(1) Blank Data - in chronological order. NOTE: This order is different from that used for samples.

(a) Tabulated results (Form I PEST).

(b) Chromatogram(s) and data system printout(s) (GC) for each GC column and instrument used for analysis, labeled as in b.(2) above.

(2) Matrix Spike Data

(a) Tabulated results (Form I PEST) of nonspike TCL compounds.

(b) Chromatogram(s) and data system printout(s) (GC), labeled as in b.(2) above.

(3) Matrix Spike Duplicate Data

(a) Tabulated results (Form I PEST) of nonspike TCL compounds.

(b) Chromatogram(s) and data system printout(s) (GC), labeled as in b.(2) above.

F. Data in Computer-Readable Form

The Contractor shall provide a computer-readable copy of the data on data reporting Forms I-X for all samples in the Sample Delivery Group, as specified in the Contract Performance/Delivery Schedule. Computer-readable data deliverables shall be submitted on IBM or IBM-compatible, 5.25 inch floppy double-sided, double density 360 K-byte or a high density 1.2 M-byte diskette.

When submitted, floppy diskettes shall be packaged and shipped in such a manner that the diskette(s) cannot be bent or folded, and will not be exposed to extreme heat or cold or any type of electromagnetic radiation. The diskette(s) must be included in the same shipment as the hardcopy data and shall, at a minimum, be enclosed in a diskette mailer.

The data shall be recorded in ASCII, text file format, and shall adhere to the file, record and field specifications listed in Exhibit H, Data Dictionary and Format for Data Deliverables in Computer-Readable Format.

If the Contractor wishes to use a reporting format other than the one specified, equivalence must be demonstrated and approved by the Project Officer prior to the award of the contract.

G. GC/MS Tapes

The Contractor must store all raw and processed GC/MS data on magnetic tape, in appropriate instrument manufacturer's format. This tape must include data for samples, blanks, matrix spikes, matrix spike duplicates, initial calibrations, continuing calibrations, BFB and DFTPP, as well as all laboratory-generated spectral libraries and quantitation reports required to generate the data package. The Contractor shall maintain a written reference logbook of tape files to EPA sample number, calibration data, standards, blanks, matrix spikes, and matrix spike duplicates. The logbook should include EPA sample numbers and standard and blank ID's, identified by Case and Sample Delivery Group.

The Contractor is required to retain the GC/MS tapes for 365 days after data submission. During that time, the Contractor shall submit tapes and associated logbook pages within seven days after receipt of a written request from the Project Officer.

H. Extracts

The Contractor shall preserve sample extracts at 4°C (±2°C) in bottles/vials with Teflon-lined septa. Extract bottles/vials shall be labeled with EPA sample number, Case number and Sample Delivery Group (SDG) number. A logbook of stored extracts shall be maintained, listing EPA sample numbers and associated Case and SDG numbers.

The Contractor is required to retain extracts for 365 days following data submission. During that time, the Contractor shall submit extracts and associated logbook pages within seven days following receipt of a written request from the Project Officer or the Sample Management Office.

I. Complete Case File Purge

(Formerly, Document Control and Chain-of-Custody Package).

The complete case file purge includes all laboratory records received or generated for a specific Case that have not been previously submitted to EPA as a deliverable. These items include but are not limited to: sample tags, custody records, sample tracking records, analysts logbook pages, bench sheets, chromatographic charts, computer printouts, raw data summaries, instrument logbook pages, correspondence, and the document inventory (see Exhibit F).

SECTION III

FORM INSTRUCTION GUIDE

This section includes specific instructions for the completion of all required forms. Each of the forms is specific to a given fraction (volatile, semivolatile, pesticide/PCB), and in some instances specific to a given matrix (water or soil) within each fraction. The contractor shall submit only those forms pertaining to the fractions analyzed for a given sample or samples. For instance, if a sample is scheduled for volatile analysis only, provide only VOA forms. There are two pages relating to the semivolatile fraction for Forms I, VI, VII, and VIII. Whenever semivolatiles are analyzed and one of the above-named forms is required, both pages (SV-1 and SV-2) must be submitted. These instructions are arranged in the following order:

A. General Information and Header Information

B. Organic Analysis Data Sheets (Form I, All Fractions)

C. Surrogate Recovery (Form II, All Fractions)

D. Matrix Spike/Matrix Spike Duplicate Recovery (Form III, All Fractions)

E. Method Blank Summary (Form IV, All Fractions)

F. GC/MS Tuning and Mass Calibration (Form V VOA, Form V SV)

G. Initial Calibration Data (Form VI VOA, Form VI SV)

H. Continuing Calibration Data (Form VII VOA, Form VII SV)

I. Internal Standard Area Summary (Form VIII VOA, Form VIII SV)

J. Pesticide Evaluation Standards Summary (Form VIII Pest)

K. Pesticide/PCB Standards Summary (Form IX Pest)

L. Pesticide/PCB Identification (Form X Pest)

A. General Information and Header Information

The data reporting forms presented in Section IV have been designed in conjunction with the computer-readable data format specified in Exhibit H, Data Dictionary and Format for Data Deliverables in Computer-Readable Format. The specific length of each variable for computer-readable data transmission purposes is given in the data dictionary (Exhibit H). Information entered on these forms must not exceed the size of the field given on the form, including such laboratory-generated items as Lab Name and Lab Sample ID.

Note that on the hardcopy forms (Section IV), the space provided for entries is greater in some instances than the length prescribed for the variable as written to diskette (see Exhibit H). Greater space is provided on the hardcopy forms for the sake of visual clarity.

Values must be reported on the hardcopy forms according to the individual form instructions in this Section. For example, results for concentrations of VOA TCL compounds must be reported to two significant figures if the value is greater than or equal to 10. Values can be written to the diskette file in any format that does not exceed the field specification as given in the record specifications and discussed in "Record Structure", paragraph 5 of Exhibit H.

All characters which appear on the data reporting forms presented in the contract (Exhibit B, Section IV) must be reproduced by the Contractor when submitting data, and the format of the forms submitted must be identical to that shown in the contract. No information may be added, deleted, or moved from its specified position without prior written approval of the EPA Project Officer. The names of the various fields and compounds (i.e., "Lab Code," "Chloromethane") must appear as they do on the forms in the contract, including the options specified in the form (i.e., "Matrix: (soil/water)" must appear, not just "Matrix"). For items appearing on the uncompleted forms (Section IV), the use of uppercase and lowercase letters is optional.

Alphabetic entries made onto the forms by the Contractor shall be in ALL UPPERCASE letters (i.e., "LOW", not "Low" or "low"). If an entry does not fill the entire blank space provided on the form, null characters shall be used to remove the remaining underscores that comprise the blank line. (See Exhibit H for more detailed instructions.) However, do not remove the underscores or vertical bar characters that delineate "boxes" on the forms. The only exception would be those underscores at the bottom of a "box" that are intended as a data entry line (for instance, see Form 2A, line 30. If data must be entered on line 30, it will replace the underscores).

Six pieces of information are common to the header sections of each data reporting form. They are: Lab Name, Contract, Lab Code, Case No., SAS No., and SDG No. This information must be entered on every form and must match on every form.

The "Lab Name" shall be the name chosen by the Contractor to identify the laboratory. It may not exceed 25 characters.

The "Lab Code" is an alphabetical abbreviation of up to 6 letters, assigned by EPA, to identify the laboratory and aid in data processing. This lab code shall be assigned by EPA at the time a contract is awarded, and shall not be modified by the Contractor, except at the direction of EPA.

The "Case No." is the EPA-assigned Case number (up to 5 digits) associated with the sample, and reported on the Traffic Report.

The "Contract" is the number of the EPA contract under which the analyses were performed.

The "SDG No." is the Sample Delivery Group number. The Sample Delivery Group (SDG) number is the EPA Sample Number of the first sample received in the SDG. When several samples are received together in the first SDG shipment, the SDG number shall be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG.

The "SAS No." is the EPA-assigned number for analyses performed under Special Analytical Services. If samples are to be analyzed under SAS only, and reported on these forms, then enter SAS No., and leave Case No. blank. If samples are analyzed according to the "Routine Analytical Services" (IFB) protocols and have additional "SAS" requirements, list both Case No. and SAS No. on all forms. If the analyses have no SAS requirements, leave "SAS No." blank. NOTE: Some samples in an SDG may have a SAS No. while others do not.

The other information common to most of the forms is the "EPA Sample No.". This number appears either in the upper righthand corner of the form, or as the left column of a table summarizing data from a number of samples. When "EPA Sample No." is entered into the triple-spaced box in the upper righthand corner of Form I or Form X, it should be entered on the middle line of the three lines that comprise the box.

All samples, matrix spikes, matrix spike duplicates, blanks and standards shall be identified with an EPA Sample Number. For samples, matrix spikes and matrix spike duplicates, the EPA Sample Number is the unique identifying number given in the Traffic Report that accompanied that sample.

In order to facilitate data assessment, the following sample suffixes must be used:

XXXXX - EPA sample number
XXXXXMS - matrix spike sample
XXXXXMSD - matrix spike duplicate sample
XXXXXRE - re-analyzed sample
XXXXXDL - sample analyzed at a secondary dilution

Form VIII Pest requires that all samples analyzed in a given 72-hour analytical sequence be specified, regardless of whether or not they are part of the SDG being reported. Therefore, use "ZZZZZ" as the EPA

Sample No. for any sample analyses not associated with the SDG being reported.

For blanks and standards, the following identification scheme must be used as the "EPA Sample No."

1. Volatile blanks shall be identified as VBLK##.

2. Semivolatile blanks shall be identified as SBLK##.

3. Pesticide/PCB blanks shall be identified as PBLK##.

The "EPA Sample No." must be unique for each blank within an SDG. Within a fraction, a laboratory must achieve this by replacing the two-character "##" terminator of the identifier with one or two characters or numbers, or a combination of both. For example, possible identifiers for volatile blanks would be VBLK1, VBLK2, VBLKA1, VBLKB2, VBLK10, VBLKAB, etc.

4. Volatile and semivolatile standards shall be identified as FSTD###, where:

   F - fraction (V for volatiles; S for semivolatiles).

   STD - indicates a standard.

   ### - the concentration in ug/L of volatile standards (i.e., 20, 50, 100, 150, and 200) or the amount injected in ng for semivolatile standards (i.e., 20, 50, 80, 120, and 160).

   As for the blank identifiers, these designations will have to be concatenated with other information to uniquely identify each standard.

5. Pesticide/PCB standards shall be identified as specified in the instructions for Form VIII.

   Several other pieces of information are common to many of the Data Reporting Forms. These include: Matrix, Sample wt/vol, Level, Lab Sample ID, and Lab File ID.

   For "Matrix" enter "SOIL" for soil/sediment samples, and enter "WATER" for water samples. NOTE: The matrix must be spelled out. Abbreviations such as "S" or "W" shall not be used.

   For "Sample wt/vol" enter the number of grams (for soil) or milliliters (for water) of sample used in the first blank line, and the units, either "G" or "ML" in the second blank.

   For "Level" enter the determination of concentration level made from the mandatory screening of soils. Enter as "LOW" or "MED", not "L" or "M". All water samples are "LOW" level and shall be entered as such.

"Lab Sample ID" is an optional laboratory-generated internal identifier. Up to 12 alpha-numeric characters may be reported here.

"Lab File ID" is the laboratory-generated name of the GC/MS data system file containing information pertaining to a particular analysis. Up to 14 alpha-numeric characters may be used here.

Forms II, IV, V, VIII, IX, and X contain a field labeled "page _ of _" in the bottom lefthand corner. If the number of entries required on any of these forms exceeds the available space, continue entries on another copy of the same fraction-specific form, duplicating all header information. If a second page is required, number them consecutively, as "page 1 of 2" and "page 2 of 2". If a second page is not required, number the page "page 1 of 1." NOTE: These forms are fraction-specific, and often matrix-specific within fraction. For example, Form II VOA-1 and Form II VOA-2 are for different data. Therefore, do not number the pages of all six versions of Form II as "1 of 6, 2 of 6, etc." Only number pages within a fraction-specific and matrix-specific form.

For rounding off numbers to the appropriate level of precision, observe the following common rules. If the figure following those to be retained is less than 5, drop it (round down). If the figure is greater than 5, drop it and increase the last digit to be retained by 1 (round up). If the figure following the last digit to be retained equals 5, round up if the digit to be retained is odd, and round down if that digit is even.

B. Organic Analysis Data Sheet (Form I)

1. Form I VOA, Form I SV-1, Form I SV-2, Form I Pest

This form is used for tabulating and reporting sample analysis results for Target Compound List (TCL) compounds. If all fractions are not requested to be analyzed, only the pages specifically required must be submitted. If VOA analysis only is requested, Form I VOA and Form I VOA TIC must be submitted. If the pesticide/PCB analysis is the only analysis requested, only Form I Pest must be submitted for that sample.

Complete the header information on each page of Form I required, according to the instructions in part A. and as follows:

For volatiles, for "% moisture not dec.", enter the nondecanted percent moisture. For semivolatiles and pesticides/PCB, enter values for both nondecanted percent moisture and decanted percent moisture, in the appropriate fields. Report percent moisture (decanted or not decanted) to the nearest whole percentage point (i.e., 5%, not 5.3%). If a decanted percent moisture is not determined, because the sample has no standing water over it, leave "% moisture dec." blank. Leave these fields blank for Form I for method blanks.

For volatiles, enter the type of GC column used in "Column: (pack/cap)." Enter "PACK" for packed columns, and "CAP" for capillary columns, whether megabore or narrow bore.

For semivolatiles and pesticides/PCBs, enter the method of extraction as "SEPF" for separatory funnel, and "CONT" for continuous liquid-liquid extraction, or "SONC" for sonication (soils only).

If gel permeation chromatography, "GPC Cleanup" was performed, enter "Y" for yes. Otherwise, enter "N" for no, if GPC was not performed.

For soil samples only, enter pH for semivolatile and pesticides/PCBs, reported to 0.1 pH units.

"Date Received" is the date of sample receipt at the laboratory, as noted on the Traffic Report (i.e., the VTSR). It should be entered as MM/DD/YY.

"Date Extracted" and "Date Analyzed" should be entered in a similar fashion. If continuous liquid-liquid extraction procedures are used, enter the date on which the procedure was started for "Date Extracted". If separatory funnel or sonication procedures are used, enter the date on which the procedure was completed. For pesticide/PCB samples, the date of analysis should be the date of the first GC analysis performed. The date of sample receipt will be compared with the extraction and analysis dates of each fraction to ensure that contract holding times were not exceeded.

If a sample has been diluted for analysis, enter the "Dilution Factor" as a single number, such as 100 for a 1 to 100 dilution of the sample. Enter 0.1 for a concentration of 10 to 1. If a sample was not diluted, enter 1.

For positively identified TCL compounds, the Contractor shall report the concentrations detected as uncorrected for blank contaminants.

For volatile and semivolatile results, report analytical results to one significant figure if the value is less than 10, and two significant figures above 10.

Report all pesticides/PCB results to two significant figures.

The appropriate concentration units, ug/L or ug/kg, must be entered.

If the result is a value greater than or equal to the quantitation limit, report the value.

Under the column labeled "Q" for qualifier, flag each result with the specific Data Reporting Qualifiers listed below. The Contractor is encouraged to use additional flags or footnotes. The definition of such flags must be explicit and must be included in the Case Narrative.

For reporting results to the USEPA, the following contract specific qualifiers are to be used. The seven qualifiers defined below are not subject to modification by the laboratory. Up to five qualifiers may be reported on Form I for each compound.

The seven EPA-defined qualifiers to be used are as follows:

U - Indicates compound was analyzed for but not detected. The sample quantitation limit must be corrected for dilution and for percent moisture. For example, 10 U for phenol in water if the sample final volume is the protocol-specified final volume. If a 1 to 10 dilution of extract is necessary, the reported limit is 100 U. For a soil sample, the value must also be adjusted for percent moisture. For example, if the sample had 24% moisture and a 1 to 10 dilution factor, the sample quantitation limit for phenol (330 U) would be corrected to:

$$\frac{(330\ U)}{D} \times df \qquad \text{where } D = \frac{100 - \%\ \text{moisture}}{100}$$

and df = dilution factor

at 24% moisture, $D = \frac{100-24}{100} = 0.76$

$$\frac{(330\ U)}{.76} \times 10 = 4300\ U$$

rounded to the appropriate number of significant figures

For soil samples subjected to GPC clean-up procedures, the CRQL is also multiplied by 2, to account for the fact that only half of the extract is recovered.

J - Indicates an estimated value. This flag is used either when estimating a concentration for tentatively identified compounds where a 1:1 response is assumed, or when the mass spectral data indicate the presence of a compound that meets the identification criteria but the result is less than the sample quantitation limit but greater than zero. For example, if the sample quantitation limit is 10 ug/L, but a concentration of 3 ug/L is calculated, report it as 3J. The sample quantitation limit must be adjusted for both dilution and percent moisture as discussed for the U flag, so that if a sample with 24% moisture and a 1 to 10 dilution factor has a calculated concentration of 300 ug/L and a sample quantitation limit of 430 ug/kg, report the concentration as 300J on Form I.

C - This flag applies to pesticide results where the identification has been confirmed by GC/MS. Single component pesticides ≥10 ng/ul in the final extract shall be confirmed by GC/MS.

B - This flag is used when the analyte is found in the associated blank as well as in the sample. It indicates possible/probable blank contamination and warns the data user to take appropriate action. This flag must be used for a TIC as well as for a positively identified TCL compound.

E - This flag identifies compounds whose concentrations exceed the calibration range of the GC/MS instrument for that specific analysis. This flag will not apply to pesticides/PCBs analyzed by GC/EC methods. If one or more compounds have a response greater than full scale, the sample or extract must be diluted and re-analyzed according to the specifications in Exhibit D. All such compounds with a response greater than full scale should have the concentration flagged with an "E" on the Form I for the original analysis. If the dilution of the extract causes any compounds identified in the first analysis to be below the calibration range in the second analysis, then the results of both analyses shall be reported on separate Forms I. The Form I for the diluted sample shall have the "DL" suffix appended to the sample number. NOTE: For total xylenes, where three isomers are quantified as two peaks, the calibration range of each peak should be considered separately, e.g., a diluted analysis is not required for total xylenes unless the concentration of either peak separately exceeds 200 ug/L.

D - This flag identifies all compounds identified in an analysis at a secondary dilution factor. If a sample or extract is re-analyzed at a higher dilution factor, as in the "E" flag above, the "DL" suffix is appended to the sample number on the Form I for the diluted sample, and all concentration values reported on that Form I are flagged with the "D" flag.

A - This flag indicates that a TIC is a suspected aldol-condensation product.

X - Other specific flags may be required to properly define the results. If used, they must be fully described and such description attached to the Sample Data Summary Package and the Case Narrative. Begin by using "X". If more than one flag is required, use "Y" and "Z", as needed. If more than five qualifiers are required for a sample result, use the "X" flag to combine several flags, as needed. For instance, the "X" flag might combine the "A", "B", and "D" flags for some sample.

The combination of flags "BU" or"UB" is expressly prohibited. Blank contaminants are flagged "B" only when they are also detected in the sample.

If analyses at two different dilution factors are required (see Exhibit D), follow the data reporting instructions given in Exhibit D and with the "D" and "E" flags above.

2. Form I VOA-TIC and Form I SV-TIC

Fill in all header information as above.

Report Tentatively Identified Compounds (TIC) including CAS number, compound name, retention time, and the estimated concentration (criteria for reporting TICs are given in Exhibit D, Section IV). Retention time must be reported in minutes and decimal minutes, not seconds or minutes:seconds.

If in the opinion of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound shall be reported as unknown.

Include a Form I VOA-TIC or SV-TIC for every volatile and semivolatile fraction of every sample and method blank analyzed, even if no TICs are found. Total the number of TICs found, including aldol-condensation products (but see below), and enter this number in the "Number TICs found." If none were found, enter "0" (zero). Form I VOA-TIC or SV-TIC must be provided for every analysis, including required dilutions and reanalyses, even if no TICs are found.

If the name of a compound exceeds the 28 spaces in the TIC column, truncate the name to 28 characters. If the compound is an unknown, restrict description to no more than 28 characters (i.e., unknown hydrocarbon, etc.).

Peaks that are suspected as aldol-condensation reaction products (i.e., 4-methyl-4-hydroxy-2-pentanone and 4-methyl-3-pentene-2-one) shall be summarized on this form, flagged "A", and included in the total "Number TICs found," but not counted as part of the 20 most intense non-TCL semivolatile compounds to be searched.

C. Surrogate Recovery (Form II)

Form II is used to report the recoveries of the surrogate compounds added to each sample, blank, matrix spike, and matrix spike duplicate. Form II is matrix-specific as well as fraction-specific, so that surrogate recoveries for volatile water samples are reported on a different version of Form II than volatile soil sample surrogate recoveries.

Complete the header information and enter EPA Sample Numbers as described in part A. For soil samples only, specify the "level" as "LOW" or "MED", as on Form I. Do not mix low and medium level samples on one form. Complete one for each level. For each surrogate, report the percent recovery to the number of significant figures given by the QC limits at the bottom of the form.

Flag each surrogate recovery outside the QC limits with an asterisk (*). The asterisk must be placed in the last space in each appropriate column, under the "#" symbol. In the far righthand column, total the number of surrogate recoveries outside the QC limits for each sample.

If no surrogates were outside the limits, enter "0".

If the surrogates are diluted out in any analysis, enter the calculated recovery or "0" (zero) if the surrogate is not detected, and flag the surrogate recoveries with a "D" in the column under the "#" symbol. Do not include results flagged "D" in the total number of recoveries for each sample outside the QC limits.

The pesticide surrogate recovery limits are only advisory, but the Contractor must flag those recoveries outside the advisory QC limits or diluted out, nonetheless.

Number all pages as described in part A.

D. Matrix Spike/Matrix Spike Duplicate Recovery (Form III)

This form is used to report the results of the analyses of a matrix spike and matrix spike duplicate. As with the surrogate recovery form (II), the form is matrix-specific within each fraction.

Complete the header information as instructed in Part A, including the EPA Sample Number for the matrix spike without the suffixes MS or MSD.

For soil samples, specify "level" as "LOW" or "MED", as on Form I. Cases containing soil samples at both levels require MS/MSD at each level, therefore, for soils, prepare one form for each level.

All water samples are "Low". Therefore, there is no MS/MSD for "medium level waters", and none shall be reported.

In the upper box in Form III, under "SPIKE ADDED", enter the calculated concentration in ug/L or ug/Kg (according to the matrix) that results from adding each spiked compound to the aliquot chosen for the matrix spike (MS). For instance, for base/neutral compounds in medium level soils, if 100 ug of spike are added to 1 g of soil, the resulting concentration is 100,000 ug/Kg. Enter the "SAMPLE CONCENTRATION", in similar units, of each spike compound detected in the original sample. If a spike compound was not detected during the analysis of the original sample, enter the sample result as "0" (zero). Under "MS CONCENTRATION", enter the actual concentration of each spike compound detected in the matrix spike aliquot. Calculate the percent recovery of each spike compound in the matrix spike aliquot to the nearest whole percent, according to Exhibit E, and enter under "MS % REC". Flag all percent recoveries outside the QC limits with an asterisk (*). The asterisk must be placed in the last space of the percent recovery column, under the "#" symbol.

Complete the lower box on Form III in a similar fashion, using the results of the analysis of the matrix spike duplicate (MSD) aliquot. Calculate the relative percent difference (RPD) between the matrix spike recovery and the matrix spike duplicate recovery, and enter this value in the lower box under "% RPD". Compare the RPDs to the QC limits given on the form, and flag each RPD outside the QC limits with an asterisk (*) in the last space of the "% RPD" column, under the "#" symbol.

Summarize the values outside the QC limits at the bottom of the page. No further action is required by the laboratory. Performance-based QC limits will be generated and updated from recovery and RPD data.

E. Method Blank Summary (Form IV)

This form summarizes the samples associated with each method blank analysis. A copy of the appropriate Form IV is required for each blank.

Complete the header information on Form IV as described in Part A.

For volatile and semivolatile blanks, enter the "Instrument ID", "Date Analyzed", "Matrix" and "Level". All water blanks are "LOW". The "Time Analyzed" shall be in military time.

For semivolatile and pesticide/PCB blanks, enter the method of extraction as "SEPF" for separatory funnel, or "SONC" for sonication, or "CONT" for continuous liquid-liquid extraction. For semivolatile and pesticide/PCB method blanks, enter the date of extraction of the blank.

Pesticide/PCB contaminants must meet the identification criteria in Exhibit D PEST, which requires analysis of the blank on two different GC Columns. Therefore, enter the date, time and instrument ID of both analyses on the pesticide method blank summary. The information on the two analyses is differentiated as Date Analyzed (1), Date Analyzed (2), etc. If the analyses were run simultaneously, the order of reporting is not important, but must be consistent with the information reported on Form X. Otherwise (1) shall be the first analysis, and (2) the second. Identify both GC columns by stationary phase under "GC Column ID". For mixed phase columns, do not enter "mixed". If the stationary phase identifier contains a manufacturer's identifier, such as "SP" or "DB", these characters may be deleted in order to fit the identifier into the 10-character field.

For Pesticide/PCB blanks, enter "Matrix" and "Level" in a similar fashion as for the other fractions. All water samples are "LOW". Enter "Lab File ID" only if GC/MS confirmation was required. Otherwise, leave blank.

For all three fractions, as appropriate, summarize the samples associated with a given method blank in the table below the header, entering EPA Sample Number, and Lab Sample ID. For volatiles, enter the Lab File ID and time of analysis of each sample. For semivolatiles, enter Lab File ID. For semivolatiles and pesticides/PCBs, enter the date of analysis of each sample. For pesticide/PCBs, if only one analysis is required (i.e., no pesticides/PCBs to be confirmed), leave blank the fields for the second analysis.

Number all pages as described in part A.

F. GC/MS Tuning and Mass Calibration (Form V)

This form is used to report the results of GC/MS tuning for volatiles and semivolatiles, and to summarize the date and time of analysis of samples, standards, blanks, matrix spikes, and matrix spike duplicates associated with each GC/MS tune.

Complete the header information as in part A. Enter the "Lab File ID" for the injection containing the GC/MS tuning compound (BFB for volatiles, DFTPP for semivolatiles). Enter the "Instrument ID". Enter the date and time of injection of the tuning compound. Enter time as military time. For volatiles, enter the matrix and level, as there are separate calibrations for water samples, low soil samples, and medium samples (see Exhibit D). For volatiles, also enter the type of GC column used as "PACK" or "CAP", under "Column."

For each ion listed on the form, enter the percent relative abundance in the righthand column. Report relative abundances to the number of significant figures given for each ion in the ion abundance criteria column.

All relative abundances must be reported as a number. If zero, enter "0", not a dash or other non-numeric character. Where parentheses appear, compute the percentage of the ion abundance of the mass given in the appropriate footnote, and enter that value in the parentheses.

In the lower half of the form, list all samples, standards, blanks, matrix spikes, and matrix spike duplicates analyzed under that tune in chronological order, by time of analysis (in military time). Refer to part A. for specific instructions for identifying standards and blanks. Enter "EPA Sample No.", "Lab Sample ID", "Lab File ID", "Date Analyzed", and "Time Analyzed" for all standards, samples, blanks, matrix spikes, and matrix spike duplicates.

The GC/MS tune expires twelve hours from the time of injection of the tuning compound (BFB or DFTPP) listed at the top of the form. In order to meet the tuning requirements, a sample, standard, blank, matrix spike, or matrix spike duplicate must be injected within twelve hours of the injection of the tuning compound.

Number all pages as described in part A.

G. Initial Calibration Data (Form VI)

After a GC/MS system has undergone an initial five-point[1] calibration at the specific concentration levels described in Exhibit E, and after all initial calibration criteria have been met, the laboratory must complete and submit a Form VI for each volatile or semivolatile TCL initial calibration performed which is relevant to the samples, blanks, matrix spikes, matrix spike duplicates in the SDG, regardless of when that calibration was performed.

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[1] For Semivolatiles, nine compounds: Benzoic Acid, 2,4-Dinitrophenol, 2,4,5-Trichlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, 4,6-Dinito-2-Methylphenol, and Pentachlorophenol will only require a four-point initial calibration at 50, 80, 120, and 160 total nanograms because detection at less than 50 nanograms per injection is difficult. If a four-point calibration is performed for these compounds, leave RF20 blank.

Complete all header information as in part A. Enter the "Case No." and "SDG No." for the current data package, regardless of the original Case for which the initial calibration was performed. Enter "Instrument ID" and the date(s) of the calibration. If the calendar date changes during the calibration procedure, the inclusive dates should be given on Form VI. For volatiles, enter matrix, level, and column, as on Form V. Enter the "Lab File ID" for each of the five calibration standards injected. Complete the response factor data for the five calibration points, and then calculate and report the average relative response factor (RRF) for all TCL and surrogate compounds. The laboratory must report the %RSD for all compounds. All CCC compounds must have a %RSD of less than or equal to 30.0 percent. All VOA SPCC compounds must have a minimum average relative response factor (RRF) of 0.300 (0.250 for Bromoform). All Semivolatile (BNA) SPCC compounds must have a minimum average relative response factor (RRF) of 0.050.

$$\%RSD = \frac{SD}{\bar{x}} \cdot x\ 100$$

where:

%RSD - Relative Standard Deviation

SD - Standard Deviation of initial 5 response factors (per compound)

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

$\bar{x}$ - mean of initial 5 response factors (per compound)

H. Continuing Calibration Data (Form VII)

The Continuing Calibration Data Form is used to verify the calibration of the GC/MS system by the analysis of specific calibration standards. A Continuing Calibration Data Form is required for each twelve (12) hour time period for both volatile and semivolatile TCL compound analyses.

The Contractor laboratory must analyze calibration standards and meet all criteria outlined in Exhibit E. After meeting specific criteria for both SPCC and CCC compounds, a Continuing Calibration Data Form must be completed and submitted.

Complete all header information as in part A. Enter instrument ID, date and time of continuing calibration, the Lab File ID of the continuing calibration standard, and date of initial calibration (give inclusive dates if initial calibration is performed over more than one date). For volatiles, enter matrix, level, and column, as on Forms V and VI. Using the appropriate Initial Calibration (Volatile or Semivolatile) fill in the average relative response factor (RRF) for each TCL compound.

Report the relative response factor (RRF50) from the continuing calibration standard analysis. Calculate the Percent Difference (%D) for all compounds. For CCC compounds, ensure that the %D is less than or equal to 25.0 percent. After this criterion has been met, report the Percent Difference for all TCL and surrogate compounds.

$$\% \text{ Difference} = \frac{\overline{RRF_I} - RRF_c}{RRF_I} \times 100$$

where,

$\overline{RRF_I}$ = average relative response factor from initial calibration.

RRF_c = relative response factor from continuing calibration standard.

All semivolatile standards are analyzed at 50 total ng.

I. Internal Standard Area Summary (Form VIII VOA and SV)

This form is used to summarize the peak areas of the internal standards added to all volatile and semivolatile samples, blanks, matrix spikes, and matrix spike duplicates. The data are used to determine when changes in internal standard responses will adversely affect quantification of target compounds. This form must be completed each time a continuing calibration is performed, or when samples are analyzed under the same GC/MS tune as an initial calibration.

Complete the header information as in part A. Enter the Lab File ID of the continuing calibration standard, as well as the date and time of analysis of the continuing calibration standard. If samples are analyzed immediately following an initial calibration, before another GC/MS tune and a continuing calibration, Form VIII shall be completed on the basis of the internal standard areas of the 50 ug/L initial calibration standard for volatiles, and the 50 ng initial calibration standard for semivolatiles. Use the date and time of analysis of this standard, and its Lab File ID and areas in place of those of a continuing calibration standard.

For volatiles, enter matrix, level, and column, as on Forms V, VI, and VII.

From the results of the analysis of the continuing calibration standard, enter the area measured for each internal standard and its retention time under the appropriate column in the row labeled "12 HOUR STD". For each internal standard, calculate the upper limit as the area of the particular standard plus 100% of its area (i.e., two times the area in the 12 HOUR STD box), and the lower limit as the area of the internal standard minus 50% of its area (i.e., one half the area in the 12 HOUR STD box). Report these values in the boxes labeled "UPPER LIMIT" and "LOWEK LIMIT" respectively.

For each sample, blank, matrix spike, and matrix spike duplicate analyzed under a given continuing calibration, enter the EPA Sample Number and the area measured for each internal standard and its retention time. If the internal standard area is outside the upper or lower limits calculated above, flag that area with an asterisk (*). The asterisk must be placed in the far right hand space of the box for each internal standard area, directly under the "#" symbol.

Number all pages as described in part A.

J. Pesticide Evaluation Standards Summary (Form VIII Pest)

This form is used to report the seventy-two (72) hour analytical sequence for pesticide analysis.

The laboratory shall complete all the header information as in Part A. Enter dates of analyses, GC column ID and Instrument ID. Identify GC Column by stationary phase. For mixed phase columns, do not enter "mixed". If the stationary phase identifier contains a manufacturer's identifier, such as "SP" or "DB", these characters may be deleted in order to fit the identifier into the 10-character field.

Evaluation Standard Mix A, B, and C must be analyzed at the initiation of every 72 hour sequence to check the linearity of the GC system. Calculate and report the Calibration Factor (total peak area[2]/amount injected in nanograms) for each of the three pesticides and the surrogate (Aldrin, Endrin, 4,4'-DDT and Dibutylchlorendate) at each concentration level (see Exhibit D). Calculate and report the percent relative standard deviation (%RSD) for each of the four compounds (Eq. 1.1). The RSD must be less than 10.0 percent for Aldrin, Endrin, and Dibutylchlorendate. The 10% RSD criteria pertain only to the column being used for quantitation, however, to determine that no pesticides/PCBs are present is a form of quantitation.

If the %RSD for 4,4'-DDT exceeds 10.C percent, plot a standard curve and determine the ng for each sample from that curve.

$$\%RSD = \frac{SD}{\bar{x}} \times 100 \qquad \text{Eq. 1.1}$$

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

$\bar{x}$ = mean of initial three Calibration factors (per compound)

Evaluation Standard Mix B must be analyzed near the beginning of the analytical sequence, after the first five samples, and then every ten samples thereafter during a 72-hour period (see Exhibits D and E).

---

[2] The term peak height may be substituted for the term peak area.

Calculate and report the percent breakdown for 4,4'-DDT and/or Endrin for the mixed phase GC column using Equations 1.2 and 1.3. (See Exhibit E). Enter the Date Analyzed and Time Analyzed for each analysis of the Evaluation Standard Mix B.

Calculate the percent breakdown for Endrin and/or 4,4'-DDT on the OV-1 or equivalent GC column using Equations 1.2 and 1.3. The combined percent breakdown must not exceed 20.0 percent for Endrin and 4,4'-DDT.

$$\% \text{ breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area}^3\text{(DDE + DDD)}}{\text{Total DDT peak area}^3\text{ (DDT + DDE + DDD)}} \times 100 \quad \text{Eq. 1.2}$$

$$\% \text{ breakdown for Endrin} = \frac{\text{Total Endrin degradation peak areas}^3\text{ (Endrin Aldehyde + Endrin Ketone)}}{\text{Total Endrin Peak Area}^3\text{(Endrin + Endrin Aldehyde + Endrin Ketone)}} \times 100 \quad \text{Eq. 1.3}$$

Enter the values for the breakdown of Endrin and 4,4'-DDT in their respective columns.

If Endrin cannot be separated from 4,4'-DDT on the OV-1 or equivalent GC column, calculate a combined percent breakdown for Endrin/4,4'-DDT using Equation 1.4. The combined degradation must not exceed 20.0 percent. Leave the endrin and 4,4'-DDT columns blank if they cannot be separated, and report only the combined breakdown.

$$\text{Combined \% breakdown} = \frac{\text{Total Endrin/DDT degradation peak area}^3\text{ (DDD, DDE, Endrin Aldehyde, Endrin Ketone)}}{\text{Total Endrin/DDT degradation peak area}^3\text{ (Endrin, Endrin Aldehyde, Endrin Ketone, DDD, DDE, DDT)}} \times 100 \quad \text{Eq. 1.4}$$

Complete the header information on the second page of Form VIII Pest as on the first page.

For each sample, standard, matrix spike, matrix spike duplicate, and blank, enter the EPA sample number, lab sample ID, date and time of analysis. Each sample analyzed as part of the 72-hour analytical sequence must be reported on the second page of Form VIII PEST even if it is not associated with the SDG, in order to determine if the proper sequence of samples and standards was followed. However, the laboratory may use the EPA Sample No. of "ZZZZZ" to distinguish all samples that are not part of the SDG being reported.

---

3 The term peak height may be substituted for the term peak area.

For pesticide/PCB standards, the following scheme shall be used to enter "EPA Sample Number".

Name	EPA Sample Number
Evaluation Mix A	EVALA
Evaluation Mix B	EVALB
Evaluation Mix C	EVALC
Individual Mix A	INDA
Individual Mix B	INDB
Toxaphene	TOXAPH
Aroclor 1016	AR1016
Aroclor 1221	AR1221
Aroclor 1232	AR1232
Aroclor 1242	AR1242
Aroclor 1248	AR1248
Aroclor 1254	AR1254
Aroclor 1260	AR1260

If Individual Mix A and Individual Mix B are combined into one mixture (see Exhibit D), the EPA Sample Number shall be entered as INDAB. Similarly, the permitted mixture of Aroclor 1016 and Aroclor 1260 shall be entered as AR1660.

Every standard, sample, matrix spike, matrix spike duplicate, and blank must contain the surrogate dibutylchlorendate (DBC) at the specified level for both water or soil/sediment samples. The retention time shift for Dibutylchlorendate on packed columns must not exceed 2.0 percent (0.3 percent for capillary columns) difference (%D) between the initial standard (Evaluation Standard Mix A) and any blank, standard, sample, matrix spike, or matrix spike duplicate analyzed during the 72-hour time period. Calculate and report the percent difference (%D) for all samples, matrix spike, matrix spike duplicate, standards, and blanks, according to Eq. 1.5.

$$\% \text{ Difference} = \frac{RT_i - RT_s}{RT_i} \times 100 \qquad \text{Eq 1.5}$$

where,

RT_i = absolute retention time of dibutylchlorendate in the initial standard (Evaluation Mixture A).

RT_s = absolute retention time of dibutylchlorendate in the sample, matrix spike, matrix spike duplicate, blank, or any standard analyzed after Evaluation Mixture A.

Enter the retention time shift for DBC in the "%D" column. Flag all those values outside the QC limits by entering an asterisk (*) in the last column, under the "*". If the retention time shift cannot be calculated due to interfering peaks, leave the %D column blank, flag the value with an asterisk, and document the problem in the Case Narrative.

Number this page as described in Part A.

Form VIII PEST is required for each seventy-two (72) hour period, for each GC system and for each GC column used to analyze TCL Pesticide/PCBs.

K. Pesticide/PCB Standards Summary (Form IX)

This form is used to monitor variations in the Calibration Factor and retention time for each pesticide/PCB standard during each seventy-two (72) hour period.

The laboratory shall complete the header information as in Part A. Enter dates of analyses, GC column ID and instrument ID. Identify GC column identification must be by stationary phase. For mixed phase columns, do not enter "mixed." If the stationary phase identifier contains a manufacturer's identifier, such as "SP" or "DB", these characters may be deleted in order to fit the identifier into the 10-character field.

Individual Standard Mix A and B must be analyzed at or near the beginning of a seventy-two (72) hour sequence (before the analysis of any samples). Individual Standard Mix A and B must also be analyzed periodically during sample analysis (at the intervals specified in Exhibits D and E), and at the end of the seventy-two (72) hour sequence. Form IX is designed to compare the first analysis of each of the standards to each subsequent analysis. Therefore, a copy of Form IX must be completed for each analysis of Individual Standard Mix A and B, and each multiresponse standard after the analysis of samples has begun. For each copy of Form IX for a given analytical sequence, the data entered in the lefthand column will be identical. The header over the lefthand column contains the inclusive dates and times of analysis of the standards reported on the left side of Form IX. Considering the first analysis of Individual Standard Mix A, Individual Mix B, and all the multiresponse pesticides and PCBs, enter the first and last dates and times of analysis of these standards. If Aroclors 1221 and 1232 are not analyzed as part of the sequence being reported, do not include the dates and times of their analyses, but do include the data on Form IX.

Report the retention time of each compound in the left hand column labeled "RT". Retention times must be reported in minutes and decimal minutes (i.e., 1.99 minutes), not in seconds, or minutes:seconds. Calculate the retention time window for each compound, according to the instructions in Exhibit E, Section III, Part 4. Report the retention time window for each compound as a range of two values, i.e., from 1.48 to 1.54. Enter the lower value of the range in the column under "RT WINDOW" labeled "FROM". Enter the upper value of the range in the column under "TO". Do not separate the two values with a hyphen, and do not enter the retention time window as a plus/minus value such as ± 0.03. NOTE: By definition, the center of the retention time window must be the retention time listed immediately to the left of the retention time window.

Calculate the calibration factor for each compound according to Equation 1.6, and the value report under the left hand column labeled "CALIBRATION FACTOR".

For each subsequent analysis of an Individual Standard Mix A or B, or a multiresponse compound, complete the right hand spaces for date and time of analysis and the EPA Sample No. for the standard (see Section J), and the columns labeled "RT" and "CALIBRATION FACTOR" with the results from that analysis. NOTE: While the lefthand side of Form IX will contain retention times, retention time windows, and calibration factors for all the compounds, the righthand side will contain data from the analysis of only some of the compounds.

$$\text{Calibration Factor} = \frac{\text{Total peak area}^4 \text{ of a Standard}}{\text{Total mass injected (ng)}} \qquad \text{Eq 1.6}$$

Calculate and report the percent difference in the Calibration Factor for each pesticide/PCB using Equation 1.7.

$$\text{Percent Difference (\%D)} = \frac{|Ab_1 - Ab_2|}{Ab_1} \times 100 \qquad \text{Eq. 1.7}$$

where,

Ab_1 = Calibration Factor from the initial standard for the 72-hour period

Ab_2 = Calibration Factor from each subsequent standard

The absolute percent difference between the individual Calibration Factors for each compound in the pesticide standard may vary no more than 15.0 percent for a quantitation run, or more than 20.0 percent for a confirmation run. Primary runs must meet the criteria required for quantitation if no other analyses are performed.

If the results of analyses of compounds in the Individual Standard Mix are to be used for quantifying pesticide/PCB concentrations in the samples preceding the analysis on the right hand side of the form, then enter "Y" for yes, in the column labeled "QNT Y/N" for each compound quantified. If the results are not used for quantitation of a particular compound, enter "N", for no. Determining that no compounds are present above the CRQL is a form of quantitation.

For each subsequent analysis of an Individual Standard Mix A or B, or multiresponse compound, complete the right hand side of a copy of Form IX, with the results of the initial analyses of all the compounds as the data in the left hand side.

For multicomponent analytes, the single largest peak characteristic of the compound must be used. A characteristic peak will not exist for similar compounds such as Aroclor 1016 and Aroclor 1242. In these cases utilization of a common peak is acceptable.

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4 The term peak height may be substituted for the term peak area.

Regardless of which standards are reported on subsequent pages of Form IX, number all pages sequentially as described in Part A. As Individual Mix A and Mix B must be analyzed at the end of an analytical sequence, there will always be at least two pages of Form IX, 1 of 2, and 2 of 2, except where Mixes A & B have been combined for capillary column analysis.

L. Pesticide/PCB Identification (Form X)

This form summarizes the tentative and confirmed identity of all TCL pesticides/PCBs detected in a given sample. It reports the retention times of the compound on both columns on which it was analyzed, as well as the retention time windows of the standard for that compound on both of these columns. One copy of Form X is required for each sample or blank in which TCL pesticides or PCBs are detected. If none are detected in a given sample, no copy of Form X is required for that sample.

Complete the header information as in Part A. Enter the GC Column ID (by stationary phase) for each of the two columns, one as GC Column (1), the other as (2). For mixed phase columns, do not enter "mixed". If the stationary phase identifier contains a manufacturer's identifier, such as "SP" or "DB", these characters may be deleted in order to fit the identifier into the 10-character field. Enter the Instrument ID associated with each GC column directly below. Enter Lab File ID only if the compounds were confirmed by GC/MS.

For each TCL pesticide or PCB detected, enter the name of the compound as it appears abbreviated on Form IX (limited to 14 characters) under "PESTICIDE/PCB". Use the abbreviations of compound names given on Form IX. Enter the retention times on each column of the compounds detected in the sample next to the appropriate column designation (1 or 2). Enter the retention time windows on each column of the appropriate standard. These data must correspond with those on Form IX, and are entered in a similar manner. The lower value is entered under the "FROM" column, the upper value under the "TO" column. Do not use a hyphen.

Under "Quant? (Y/N)" enter "Y" for the GC column (1 or 2) used for quantitation, and "N" for the other column, for each compound. Do not leave this field blank for either GC column.

Under "GC/MS? (Y/N)" enter "Y" for both GC columns if the compound was confirmed by GC/MS. Enter "N" for both GC columns if the compound was not confirmed by GC/MS.

If more Pesticide/PCB TCL compounds are identified in an individual sample than can be reported on one copy of Form X, then complete as many additional copies of Form X as necessary, duplicating all header information, and numbering the pages as described in Part A.

1A
VOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Level: (low/med) _____ Date Received: _____

% Moisture: not dec._____ Date Analyzed: _____

Column: (pack/cap) _____ Dilution Factor: _____

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/Kg)_____	Q
74-87-3	Chloromethane		
74-83-9	Bromomethane		
75-01-4	Vinyl Chloride		
75-00-3	Chloroethane		
75-09-2	Methylene Chloride		
67-64-1	Acetone		
75-15-0	Carbon Disulfide		
75-35-4	1,1-Dichloroethene		
75-34-3	1,1-Dichloroethane		
540-59-0	1,2-Dichloroethene (total)		
67-66-3	Chloroform		
107-06-2	1,2-Dichloroethane		
78-93-3	2-Butanone		
71-55-6	1,1,1-Trichloroethane		
56-23-5	Carbon Tetrachloride		
108-05-4	Vinyl Acetate		
75-27-4	Bromodichloromethane		
78-87-5	1,2-Dichloropropane		
10061-01-5	cis-1,3-Dichloropropene		
79-01-6	Trichloroethene		
124-48-1	Dibromochloromethane		
79-00-5	1,1,2-Trichloroethane		
71-43-2	Benzene		
10061-02-6	trans-1,3-Dichloropropene		
75-25-2	Bromoform		
108-10-1	4-Methyl-2-Pentanone		
591-78-6	2-Hexanone		
127-18-4	Tetrachloroethene		
79-34-5	1,1,2,2-Tetrachloroethane		
108-88-3	Toluene		
108-90-7	Chlorobenzene		
100-41-4	Ethylbenzene		
100-42-5	Styrene		
1330-20-7	Xylene (total)		

1B

SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Lab Sample ID: _____

Sample wt/vol: _____ (g/mL) ____ Lab File ID: _____

Level: (low/med) _____ Date Received: _____

% Moisture: not dec. _____ dec. _____ Date Extracted: _____

Extraction: (SepF/Cont/Sonc) _____ Date Analyzed: _____

GPC Cleanup: (Y/N) ___ pH: ____ Dilution Factor: _____

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/Kg) _____	Q
108-95-2	Phenol		
111-44-4	bis(2-Chloroethyl)ether		
95-57-8	2-Chlorophenol		
541-73-1	1,3-Dichlorobenzene		
106-46-7	1,4-Dichlorobenzene		
100-51-6	Benzyl alcohol		
95-50-1	1,2-Dichlorobenzene		
95-48-7	2-Methylphenol		
108-60-1	bis(2-Chloroisopropyl)ether		
106-44-5	4-Methylphenol		
621-64-7	N-Nitroso-di-n-propylamine		
67-72-1	Hexachloroethane		
98-95-3	Nitrobenzene		
78-59-1	Isophorone		
88-75-5	2-Nitrophenol		
105-67-9	2,4-Dimethylphenol		
65-85-0	Benzoic acid		
111-91-1	bis(2-Chloroethoxy)methane		
120-83-2	2,4-Dichlorophenol		
120-82-1	1,2,4-Trichlorobenzene		
91-20-3	Naphthalene		
106-47-8	4-Chloroaniline		
87-68-3	Hexachlorobutadiene		
59-50-7	4-Chloro-3-methylphenol		
91-57-6	2-Methylnaphthalene		
77-47-4	Hexachlorocyclopentadiene		
88-06-2	2,4,6-Trichlorophenol		
95-95-4	2,4,5-Trichlorophenol		
91-58-7	2-Chloronaphthalene		
88-74-4	2-Nitroaniline		
131-11-3	Dimethylphthalate		
208-96-8	Acenaphthylene		
606-20-2	2,6-Dinitrotoluene		

1C

SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: (soil/water)_____ Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Level: (low/med) _____ Date Received: _____

% Moisture: not dec._____ dec._____ Date Extracted:_____

Extraction: (SepF/Cont/Sonc) _____ Date Analyzed: _____

GPC Cleanup: (Y/N)___ pH:____ Dilution Factor: _____

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/Kg)_____	Q
99-09-2	3-Nitroaniline		
83-32-9	Acenaphthene		
51-28-5	2,4-Dinitrophenol		
100-02-7	4-Nitrophenol		
132-64-9	Dibenzofuran		
121-14-2	2,4-Dinitrotoluene		
84-66-2	Diethylphthalate		
7005-72-3	4-Chlorophenyl-phenylether		
86-73-7	Fluorene		
100-01-6	4-Nitroaniline		
534-52-1	4,6-Dinitro-2-methylphenol		
86-30-6	N-Nitrosodiphenylamine (1)		
101-55-3	4-Bromophenyl-phenylether		
118-74-1	Hexachlorobenzene		
87-86-5	Pentachlorophenol		
85-01-8	Phenanthrene		
120-12-7	Anthracene		
84-74-2	Di-n-butylphthalate		
206-44-0	Fluoranthene		
129-00-0	Pyrene		
85-68-7	Butylbenzylphthalate		
91-94-1	3,3'-Dichlorobenzidine		
56-55-3	Benzo(a)anthracene		
218-01-9	Chrysene		
117-81-7	bis(2-Ethylhexyl)phthalate		
117-84-0	Di-n-octylphthalate		
205-99-2	Benzo(b)fluoranthene		
207-08-9	Benzo(k)fluoranthene		
50-32-8	Benzo(a)pyrene		
193-39-5	Indeno(1,2,3-cd)pyrene		
53-70-3	Dibenz(a,h)anthracene		
191-24-2	Benzo(g,h,i)perylene		

(1) - Cannot be separated from Diphenylamine

1E

VOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

EPA SAMPLE NO.

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: (soil/water)_____ Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Level: (low/med) _____ Date Received: _____

% Moisture: not dec._____ Date Analyzed: _____

Column: (pack/cap) _____ Dilution Factor: _____

Number TICs found: _____ CONCENTRATION UNITS: (ug/L or ug/Kg)_____

	CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.					
2.					
3.					
4.					
5.					
6.					
7.					
8.					
9.					
10.					
11.					
12.					
13.					
14.					
15.					
16.					
17.					
18.					
19.					
20.					
21.					
22.					
23.					
24.					
25.					
26.					
27.					
28.					
29.					
30.					

1F

SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

EPA SAMPLE NO.

Lab Name:_____ Contract:_____

La_ Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: (soil/water)_____ Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Level: (low/med) _____ Date Received: _____

% Moisture: not dec._____ dec._____ Date Extracted:_____

Extraction: (SepF/Cont/Sonc) _____ Date Analyzed: _____

GPC Cleanup: (Y/N)___ pH:____ Dilution Factor: _____

Number TICs found: _____ CONCENTRATION UNITS: (ug/L or ug/Kg)_____

	CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.					
2.					
3.					
4.					
5.					
6.					
7.					
8.					
9.					
10.					
11.					
12.					
13.					
14.					
15.					
16.					
17.					
18.					
19.					
20.					
21.					
22.					
23.					
24.					
25.					
26.					
27.					
28.					
29.					
30.					

2A
WATER VOLATILE SURROGATE RECOVERY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

	EPA SAMPLE NO.	S1 (TOL) #	S2 (BFB) #	S3 (DCE) #	OTHER	TOT OUT
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						

	QC LIMITS
S1 (TOL) = Toluene-d8	(88-110)
S2 (BFB) = Bromofluorobenzene	(86-115)
S3 (DCE) = 1,2-Dichloroethane-d4	(76-114)

Column to be used to flag recovery values

* Values outside of contract required QC limits

D Surrogates diluted out

2B
SOIL VOLATILE SURROGATE RECOVERY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Level: (low/med) _____

	EPA SAMPLE NO.	S1 (TOL) #	S2 (BFB) #	S3 (DCE) #	OTHER	TOT OUT
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						

	QC LIMITS
S1 (TOL) = Toluene-d8	(81-117)
S2 (BFB) = Bromofluorobenzene	(74-121)
S3 (DCE) = 1,2-Dichloroethane-d4	(70-121)

Column to be used to flag recovery values

* Values outside of contract required QC limits

D Surrogates diluted out

page __ of __

2C
WATER SEMIVOLATILE SURROGATE RECOVERY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

	EPA SAMPLE NO.	S1 (NBZ) #	S2 (FBP) #	S3 (TPH) #	S4 (PHL) #	S5 (2FP) #	S6 (TBP) #	OTHER	TOT OUT
01									
02									
03									
04									
05									
06									
07									
08									
09									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29									
30									

	QC LIMITS
S1 (NBZ) = Nitrobenzene-d5	(35-114)
S2 (FBP) = 2-Fluorobiphenyl	(43-116)
S3 (TPH) = Terphenyl-d14	(33-141)
S4 (PHL) = Phenol-d6	(10-94)
S5 (2FP) = 2-Fluorophenol	(21-100)
S6 (TBP) = 2,4,6-Tribromophenol	(10-123)

Column to be used to flag recovery values
* Values outside of contract required QC limits
D Surrogates diluted out

2D

SOIL SEMIVOLATILE SURROGATE RECOVERY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Level: (low/med)_____

	EPA SAMPLE NO.	S1 (NBZ) #	S2 (FBP) #	S3 (TPH) #	S4 (PHL) #	S5 (2FP) #	S6 (TBP) #	OTHER	TOT OUT
01									
02									
03									
04									
05									
06									
07									
08									
09									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29									
30									

		QC LIMITS
S1 (NBZ)	= Nitrobenzene-d5	(23-120)
S2 (FBP)	= 2-Fluorobiphenyl	(30-115)
S3 (TPH)	= Terphenyl-d14	(18-137)
S4 (PHL)	= Phenol-d6	(24-113)
S5 (2FP)	= 2-Fluorophenol	(25-121)
S6 (TBP)	= 2,4,6-Tribromophenol	(19-122)

Column to be used to flag recovery values
* Values outside of contract required QC limits
D Surrogates diluted out

page __ of __

3A

WATER VOLATILE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix Spike - EPA Sample No.: _____

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONCENTRATION (ug/L)	MS CONCENTRATION (ug/L)	MS % REC #	QC LIMI REC.
1,1-Dichloroethene					61-14
Trichloroethene					71-12
Benzene					76-12
Toluene					76-12
Chlorobenzene					75-13

COMPOUND	SPIKE ADDED (ug/L)	MSD CONCENTRATION (ug/L)	MSD % REC #	% RPD #	QC LIMITS RPD	QC LIMITS REC.
1,1-Dichloroethene					14	61-14
Trichloroethene					14	71-12
Benzene					11	76-12
Toluene					13	76-12
Chlorobenzene					13	75-13

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

RPD:_____ out of _____ outside limits
Spike Recovery:_____ out of _____ outside limits

COMMENTS: _____

3B

SOIL VOLATILE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix Spike - EPA Sample No.: _____ Level:(low/med) _____

COMPOUND	SPIKE ADDED (ug/Kg)	SAMPLE CONCENTRATION (ug/Kg)	MS CONCENTRATION (ug/Kg)	MS % REC #	QC LIMI REC
1,1-Dichloroethene					59-1
Trichloroethene					62-1
Benzene					66-1
Toluene					59-1
Chlorobenzene					60-1

COMPOUND	SPIKE ADDED (ug/Kg)	MSD CONCENTRATION (ug/Kg)	MSD % REC #	% RPD #	QC LIMITS RPD	REC.
1,1-Dichloroethene					22	59-17
Trichloroethene					24	62-13
Benzene					21	66-14
Toluene					21	59-13
Chlorobenzene					21	60-13

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

RPD:_____ out of _____ outside limits
Spike Recovery:_____ out of _____ outside limits

COMMENTS: _____

3C
WATER SEMIVOLATILE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix Spike - EPA Sample No.: _____

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONCENTRATION (ug/L)	MS CONCENTRATION (ug/L)	MS % REC #	QC LIMIT REC
Phenol					12-,
2-Chlorophenol					27-12
1,4-Dichlorobenzene					36- 9
N-Nitroso-di-n-prop.(1)					41-1
1,2,4-Trichlorobenzene					39- 9
4-Chloro-3-methylphenol					23- 9
Acenaphthene					46-1
4-Nitrophenol					10- 8
2,4-Dinitrotoluene					24- 9
Pentachlorophenol					9-1
Pyrene					26-12

COMPOUND	SPIKE ADDED (ug/L)	MSD CONCENTRATION (ug/L)	MSD % REC #	% RPD #	QC LIMITS RPD	QC LIMITS REC.
Phenol					42	12- 8
2-Chlorophenol					40	27-12
1,4-Dichlorobenzene					28	36- 9
N-Nitroso-di-n-prop.(1)					38	41-11
1,2,4-Trichlorobenzene					28	39- 9
4-Chloro-3-methylphenol					42	23- 9
Acenaphthene					31	46-11
4-Nitrophenol					50	10- 8
2,4-Dinitrotoluene					38	24- 9
Pentachlorophenol					50	9-10
Pyrene					31	26-12

(1) N-Nitroso-di-n-propylamine

Column to be used to flag recovery and RPD values with an asterisk
* Values outside of QC limits

RPD:_____ out of _____ outside limits
Spike Recovery:_____ out of _____ outside limits

COMMENTS: _____

3D

SOIL SEMIVOLATILE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix Spike - EPA Sample No.: _____ Level:(low/med) _____

COMPOUND	SPIKE ADDED (ug/Kg)	SAMPLE CONCENTRATION (ug/Kg)	MS CONCENTRATION (ug/Kg)	MS % REC #	QC LIMITS REC.
Phenol					26- 9
2-Chlorophenol					25-10
1,4-Dichlorobenzene					28-10
N-Nitroso-di-n-prop.(1)					41-12
1,2,4-Trichlorobenzene					38-10
4-Chloro-3-methylphenol					26-10
Acenaphthene					31-13
4-Nitrophenol					11-11
2,4-Dinitrotoluene					28- 8
Pentachlorophenol					17-10
Pyrene					35-14

COMPOUND	SPIKE ADDED (ug/Kg)	MSD CONCENTRATION (ug/Kg)	MSD % REC #	% RPD #	QC LIMITS RPD	QC LIMITS REC.
Phenol					35	26- 90
2-Chlorophenol					50	25-102
1,4-Dichlorobenzene					27	28-104
N-Nitroso-di-n-prop.(1)					38	41-126
1,2,4-Trichlorobenzene					23	38-107
4-Chloro-3-methylphenol					33	26-103
Acenaphthene					19	31-137
4-Nitrophenol					50	11-114
2,4-Dinitrotoluene					47	28- 89
Pentachlorophenol					47	17-109
Pyrene					36	35-142

(1) N-Nitroso-di-n-propylamine

Column to be used to flag recovery and RPD values with an asterisk
* Values outside of QC limits

RPD:_____ out of _____ outside limits
Spike Recovery:_____ out of _____ outside limits

COMMENTS: _____

4A
VOLATILE METHOD BLANK SUMMARY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Lab File ID: _____ Lab Sample ID: _____

Date Analyzed: _____ Time Analyzed: _____

Matrix: (soil/water) _____ Level:(low/med) _____

Instrument ID: _____

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	TIME ANALYZED
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				
27				
28				
29				
30				

COMMENTS: _____

page __ of __

4B
SEMIVOLATILE METHOD BLANK SUMMARY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Lab File ID: _____ Lab Sample ID: _____

Date Extracted: _____ Extraction: (SepF/Cont/Sonc) _____

Date Analyzed: _____ Time Analyzed: _____

Matrix: (soil/water) _____ Level: (low/med) _____

Instrument ID: _____

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				
27				
28				
29				
30				

COMMENTS: _____

4C
PESTICIDE METHOD BLANK SUMMARY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Lab Sample ID: _____ Lab File ID: _____

Matrix:(soil/water) _____ Level:(low/med) _____

Date Extracted: _____ Extraction: (SepF/Cont/Sonc)_____

Date Analyzed (1): _____ Date Analyzed (2): _____

Time Analyzed (1): _____ Time Analyzed (2): _____

Instrument ID (2): _____ Instrument ID (2): _____

GC Column ID (1): _____ GC Column ID (1): _____

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	EPA SAMPLE NO.	LAB SAMPLE ID	DATE ANALYZED 1	DATE ANALYZED 2
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				

COMMENTS: _____

5A
VOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION - BROMOFLUOROBENZENE (BFB)

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Lab File ID: _____ BFB Injection Date:_____

Instrument ID: _____ BFB Injection Time:_____

Matrix:(soil/water) _____ Level:(low/med) _____ Column:(pack/cap) _____

m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
50	15.0 - 40.0% of mass 95	
75	30.0 - 60.0% of mass 95	
95	Base peak, 100% relative abundance	
96	5.0 - 9.0% of mass 95	
173	Less than 2.0% of mass 174	( )1
174	Greater than 50.0% of mass 95	
175	5.0 - 9.0% of mass 174	( )1
176	Greater than 95.0%, but less than 101.0% of mass 174	( )1
177	5.0 - 9.0% of mass 176	( )2

1-Value is % mass 174 2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS, MSD, BLANKS, AND STANDARDS:

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED	TIME ANALYZED
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					

page __ of __

5B
SEMIVOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION - DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP)

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Lab File ID: _____ DFTPP Injection Date:_____

Instrument ID: _____ DFTPP Injection Time:_____

m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
51	30.0 - 60.0% of mass 198	
68	Less than 2.0% of mass 69	_____( )1
69	Mass 69 relative abundance	
70	Less than 2.0% of mass 69	_____( )1
127	40.0 - 60.0% of mass 198	
197	Less than 1.0% of mass 198	
198	Base Peak, 100% relative abundance	
199	5.0 to 9.0% of mass 198	
275	10.0 - 30.0% of mass 198	
365	Greater than 1.00% of mass 198	
441	Present, but less than mass 443	
442	Greater than 40.0% of mass 198	
443	17.0 - 23.0% of mass 442	_____( )2

1-Value is % mass 69 2-Value is % mass 442

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS, MSD, BLANKS, AND STANDARDS:

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED	TIME ANALYZED
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					

VOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Date(s):_____ _____

Matrix:(soil/water) _____ Level:(low/med) _____ Column:(pack/cap) _____

Min $\overline{RRF}$ for SPCC(#) = 0.300 (0.250 for Bromoform) Max %RSD for CCC(*) = 30.0

LAB FILE ID: RRF20 = _____ RRF50 = _____
RRF100= _____ RRF150= _____ RRF200= _____

COMPOUND	RRF20	RRF50	RRF100	RRF150	RRF200	$\overline{RRF}$	%RSD
Chloromethane	#						
Bromomethane							
Vinyl Chloride	*						
Chloroethane							
Methylene Chloride							
Acetone							
Carbon Disulfide							
1,1-Dichloroethene	*						
1,1-Dichloroethane	#						#
1,2-Dichloroethene (total)							
Chloroform	*						
?-Dichloroethane							
2-Butanone							
1,1,1-Trichloroethane							
Carbon Tetrachloride							
Vinyl Acetate							
Bromodichloromethane							
1,2-Dichloropropane	*						
cis-1,3-Dichloropropene							*
Trichloroethene							
Dibromochloromethane							
1,1,2-Trichloroethane							
Benzene							
trans-1,3-Dichloropropene							
Bromoform	#						#
4-Methyl-2-Pentanone							
2-Hexanone							
Tetrachloroethene							
1,1,2,2-Tetrachloroethane	#						
Toluene	*						*
Chlorobenzene	#						#
Ethylbenzene	*						*
Styrene							
Xylene (total)							
Toluene-d8							
?romofluorobenzene							
1,2-Dichloroethane-d4							

6B

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Date(s):_____ _____

Min $\overline{RRF}$ for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0

LAB FILE ID: RRF20 =_____ RRF50 =_____
RRF80 =_____ RRF120=_____ RRF160=_____

COMPOUND	RRF20	RRF50	RRF80	RRF120	RRF160	$\overline{RRF}$	% RSD
Phenol	*						
bis(2-Chloroethyl)ether							
2-Chlorophenol							
1,3-Dichlorobenzene							
1,4-Dichlorobenzene	*						
Benzyl alcohol							
1,2-Dichlorobenzene							
2-Methylphenol							
bis(2-Chloroisopropyl)ether							
4-Methylphenol							
N-Nitroso-di-n-propylamine	#						
Hexachloroethane							
Nitrobenzene							
Isophorone							
2-Nitrophenol	*						
2,4-Dimethylphenol							
Benzoic acid							
bis(2-Chloroethoxy)methane							
2,4-Dichlorophenol	*						
1,2,4-Trichlorobenzene							
Naphthalene							
4-Chloroaniline							
Hexachlorobutadiene	*						
4-Chloro-3-methylphenol	*						
2-Methylnaphthalene							
Hexachlorocyclopentadiene	#						
2,4,6-Trichlorophenol	*						
2,4,5-Trichlorophenol							
2-Chloronaphthalene							
2-Nitroaniline							
Dimethylphthalate							
Acenaphthylene							
2,6-Dinitrotoluene							
3-Nitroaniline							
Acenaphthene	*						
2,4-Dinitrophenol	#						
4-Nitrophenol	#						

6C
SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Date(s):_____ _____

Min $\overline{RRF}$ for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.

LAB FILE ID: RRF20 = _____ RRF50 = _____
RRF80 = _____ RRF120= _____ RRF160= _____

COMPOUND	RRF20	RRF50	RRF80	RRF120	RRF160	$\overline{RRF}$	% RSD
Dibenzofuran							
2,4-Dinitrotoluene							
Diethylphthalate							
4-Chlorophenyl-phenylether							
Fluorene							
4-Nitroaniline							
4,6-Dinitro-2-methylphenol							
N-Nitrosodiphenylamine (1) *							
4-Bromophenyl-phenylether							
Hexachlorobenzene							
Pentachlorophenol *							
Phenanthrene							
thracene							
Di-n-butylphthalate							
Fluoranthene *							
Pyrene							
Butylbenzylphthalate							
3,3'-Dichlorobenzidine							
Benzo(a)anthracene							
Chrysene							
bis(2-Ethylhexyl)phthalate							
Di-n-octylphthalate *							
Benzo(b)fluoranthene							
Benzo(k)fluoranthene							
Benzo(a)pyrene *							
Indeno(1,2,3-cd)pyrene							
Dibenz(a,h)anthracene							
Benzo(g,h,i)perylene							
Nitrobenzene-d5							
2-Fluorobiphenyl							
Terphenyl-d14							
Phenol-d6							
2-Fluorophenol							
2,4,6-Tribromophenol							

(Cannot be separated from Diphenylamine

7A

VOLATILE CONTINUING CALIBRATION CHECK

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Date:_____ Time:_____

Lab File ID: _____ Init. Calib. Date(s):_____ _____

Matrix:(soil/water) _____ Level:(low/med) _____ Column:(pack/cap) _____

Min RRF50 for SPCC(#) = 0.300 (0.250 for Bromoform) Max %D for CCC(*) = 25.0%

COMPOUND	$\overline{RRF}$	RRF50	%D
Chloromethane	#			#
Bromomethane				
Vinyl Chloride	*			*
Chloroethane				
Methylene Chloride				
Acetone				
Carbon Disulfide				
1,1-Dichloroethene	*			*
1,1-Dichloroethane	#			#
1,2-Dichloroethene (total)				
Chloroform	*			*
1,2-Dichloroethane				
2-Butanone				
1,1,1-Trichloroethane				
Carbon Tetrachloride				
Vinyl Acetate				
Bromodichloromethane				
1,2-Dichloropropane	*			*
cis-1,3-Dichloropropene				
Trichloroethene				
Dibromochloromethane				
1,1,2-Trichloroethane				
Benzene				
trans-1,3-Dichloropropene				
Bromoform	#			#
4-Methyl-2-Pentanone				
2-Hexanone				
Tetrachloroethene				
1,1,2,2-Tetrachloroethane	#			#
Toluene	*			*
Chlorobenzene	#			#
Ethylbenzene	*			*
Styrene				
Xylene (total)				
Toluene-d8				
Bromofluorobenzene				
1,2-Dichloroethane-d4				

SEMIVOLATILE CONTINUING CALIBRATION CHECK

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Date:_____ Time:_____

Lab File ID: _____ Init. Calib. Date(s):_____ _____

Min RRF50 for SPCC(#) = 0.050 Max %D for CCC(*) = 25.0%

COMPOUND	$\overline{RRF}$	RRF50	%D
Phenol *			*
bis(2-Chloroethyl)ether			
2-Chlorophenol			
1,3-Dichlorobenzene			
1,4-Dichlorobenzene *			*
Benzyl alcohol			
1,2-Dichlorobenzene			
2-Methylphenol			
bis(2-Chloroisopropyl)ether			
4-Methylphenol			
N-Nitroso-di-n-propylamine #			#
Hexachloroethane			
Nitrobenzene			
Isophorone			
2-Nitrophenol *			*
2,4-Dimethylphenol			
Benzoic acid			
bis(2-Chloroethoxy)methane			
2,4-Dichlorophenol *			*
1,2,4-Trichlorobenzene			
Naphthalene			
4-Chloroaniline			
Hexachlorobutadiene *			*
4-Chloro-3-methylphenol *			*
2-Methylnaphthalene			
Hexachlorocyclopentadiene #			#
2,4,6-Trichlorophenol *			*
2,4,5-Trichlorophenol			
2-Chloronaphthalene			
2-Nitroaniline			
Dimethylphthalate			
Acenaphthylene			
2,6-Dinitrotoluene			
3-Nitroaniline			
Acenaphthene *			*
2,4-Dinitrophenol #			#
4-Nitrophenol #			#

SEMIVOLATILE CONTINUING CALIBRATION CHECK

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Date:_____ Time:_____

Lab File ID: _____ Init. Calib. Date(s):_____ _____

Min RRF50 for SPCC(#) = 0.050 Max %D for CCC(*) = 25.0

COMPOUND	$\overline{RRF}$	RRF50	%D
Dibenzofuran			
2,4-Dinitrotoluene			
Diethylphthalate			
4-Chlorophenyl-phenylether			
Fluorene			
4-Nitroaniline			
4,6-Dinitro-2-methylphenol			
N-Nitrosodiphenylamine (1) *			*
4-Bromophenyl-phenylether			
Hexachlorobenzene			
Pentachlorophenol *			*
Phenanthrene			
Anthracene			
Di-n-butylphthalate			
Flucranthene *			*
Pyrene			
Butylbenzylphthalate			
3,3'-Dichlorobenzidine			
Benzo(a)anthracene			
Chrysene			
bis(2-Ethylhexyl)phthalate			
Di-n-octylphthalate *			*
Benzo(b)fluoranthene			
Benzo(k)fluoranthene			
Benzo(a)pyrene *			*
Indeno(1,2,3-cd)pyrene			
Dibenz(a,h)anthracene			
Benzo(g,h,i)perylene			
Nitrobenzene-d5			
2-Fluorobiphenyl			
Terphenyl-d14			
Phenol-d6			
2-Fluorophenol			
2,4,6-Tribromophenol			

(1) Cannot be separated from Diphenylamine

8A
VOLATILE INTERNAL STANDARD AREA SUMMARY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Lab File ID (Standard): _____ Date Analyzed:_____

Instrument ID: _____ Time Analyzed:_____

Matrix:(soil/water) _____ Level:(low/med) _____ Column:(pack/cap) _____

	IS1(BCM) AREA #	RT	IS2(DFB) AREA #	RT	IS3(CBZ) AREA #	RT
12 HOUR STD						
UPPER LIMIT						
LOWER LIMIT						
EPA SAMPLE NO.						
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						

IS1 (BCM) = Bromochloromethane
IS2 (DFB) = 1,4-Difluorobenzene
IS3 (CBZ) = Chlorobenzene-d5

UPPER LIMIT = + 100% of internal standard area.
LOWER LIMIT = - 50% of internal standard area.

Column used to flag internal standard area values with an asterisk

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8B

SEMIVOLATILE INTERNAL STANDARD AREA SUMMARY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Lab File ID (Standard): _____ Date Analyzed:_____

Instrument ID: _____ Time Analyzed:_____

	IS1(DCB) AREA #	RT	IS2(NPT) AREA #	RT	IS3(ANT) AREA #	RT
12 HOUR STD						
UPPER LIMIT						
LOWER LIMIT						
EPA SAMPLE NO.						
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						

IS1 (DCB) = 1,4-Dichlorobenzene-d4
IS2 (NPT) = Naphthalene-d8
IS3 (ANT) = Acenaphthene-d10

UPPER LIMIT = + 100% of internal standard area.
LOWER LIMIT = - 50% of internal standard area.

Column used to flag internal standard area values with an asterisk

SEMIVOLATILE INTERNAL STANDARD AREA SUMMARY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Lab File ID (Standard): _____ Date Analyzed:_____

Instrument ID: _____ Time Analyzed:_____

	IS4(PHN) AREA #	RT	IS5(CRY) AREA #	RT	IS6(PRY) AREA #	RT
12 HOUR STD						
UPPER LIMIT						
LOWER LIMIT						
EPA SAMPLE NO.						
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						

IS4 (PHN) = Phenanthrene-d10
IS5 (CRY) = Chrysene-d12
IS6 (PRY) = Perylene-d12

UPPER LIMIT = + 100% of internal standard area.
LOWER LIMIT = - 50% of internal standard area.

Column used to flag internal standard area values with an asterisk

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INTERIM CHANGE NOTICE
(ICN)

ICN-PNL-ALO-360.1, R0
Page 1 of 1

A. Document Number: PNL-ALO-360 Revision Number: 0
Document Title: Florisil Column Cleanup
Document's Original Author: EW Hoppe

Effective Date of ICN: 09/06/91

Change Requested By: SM Panther

B. Action

Change "PNL-ALO-361" on page 1 of attachment 1 to "PNL-ALO-360".

Pen and ink corrections on original.

C. Effect of Change

None

D. Reason for Change/Description of Change

Correction of typographical error.

E. Approval Signatures

(Please sign and date)

Type of Change: {Check (✓) one}

☒ Minor Change ☐ Major Change

Process Quality Department: _____ Date: 9/6/91

Approval Authority: _____ Date: 9/9/91

Other Approvals: _____ Date: 9/6/91

: _____ Date: __/__/__

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-360, FLORISIL™ COLUMN CLEANUP FOR PESTICIDES/PCBs ANALYSIS

APPLICABILITY

This procedure provides an alternate to the alumina column cleanup of the extract solution that is produced according to procedure PNL-ALO-347 for the analysis of pesticide and PCB compounds. The Florisil™ is a good complement to alumina, it is less subject to deactivation, and it provides more consistent results in the analysis.

DEFINITIONS

None

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

PROCEDURE

See Attachment 1 for the detailed procedure. This procedure is the USEPA SW-846 Method 3620.

QUALITY CONTROL

See Attachment 1 of Method PNL-ALO-347 for the detailed quality control procedure. The use of the Florisil™ may affect the surrogate and matrix spike recoveries.

REFERENCES

USEPA Test Methods for Evaluating Solid Wastes, SW-846, Volume IB, Method 3620 and Chapter 1, November, 1986.

PNL-ALO-347, Sample Preparation for Pesticides/PCBs Analysis in Water and Soil/Sediment.

Author	Date	Project Mgr.	Date	QAD Representative	Date
[signature]	1-30-91	B.M Gillespie	1-30-91	[signature]	1/31/91
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
[signature]	1-30-91	[signature]	1-31-91		

Procedure No.	Revision No.	Effective Date	Page	of
PNL-ALO-360	0	APR 26 1991	1	1

METHOD 3620

FLORISIL COLUMN CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Florisil, a registered tradename of the Floridin Co., is a magnesium silicate with acidic properties. It is used for general column chromatography as a cleanup procedure prior to sample analysis by gas chromatography.

1.2 General applications: Cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes (Floridin). Additionally, Florisil is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates (Gordon and Ford).

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing the following analyte groups: phthalate esters; nitrosamines; organochlorine pesticides; nitroaromatics; haloethers; chlorinated hydrocarbons; and organophosphorous pesticides.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Beaker: 500-mL.

4.2 Chromatographic column: 300-mm long x 10-mm I.D. or 400-mm long x 20-mm I.D., to be specified in Paragraph 7.0; with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits

may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Muffle furnace.

4.5 Reagent bottle: 500-mL.

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.8 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

5.1 Florisil: Pesticide residue (PR) grade (60/100 mesh); purchase-activated at 1250°F (677°C), stored in glass containers with ground-glass stoppers or foil-lined screw caps.

5.1.1 **Deactivation of Florisil:** for cleanup of phthalate esters. To prepare for use, place 100 g of Florisil into a 500-mL beaker and heat for approximately 16 hr at 40°C. After heating, transfer to a 500-mL reagent bottle. Tightly seal and cool to room temperature. When cool add 3 mL of reagent water. Mix thoroughly by shaking or rolling for 10 min and let stand for at least 2 hr. Keep the bottle sealed tightly.

5.1.2 **Activation of Florisil:** for cleanup of nitrosamines, organochlorine pesticides and PCBs, nitroaromatics, haloethers, chlorinated hydrocarbons, and organophosphorous pesticides. Just before use, activate each batch at least 16 hr at 130°C in a glass container loosely covered with aluminum foil. Alternatively, store the Florisil in an oven at 130°C. Cool the Florisil before use in a desiccator.

(Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g (Mills).)

5.2 Sodium sulfate (ACS): Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.3 Eluting solvents:

5.3.1 **Diethyl ether:** Pesticide quality or equivalent.

5.3.1.1 Must be free of peroxides as indicated by EM Quant test strips (available from EM Laboratories Inc., 500 Executive Boulevard, Elmsford, NY 10523).

5.3.1.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

5.3.2 **Acetone; hexane; methylene chloride; pentane; petroleum ether** (boiling range 30-60°C): Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Phthalate esters:

7.1.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.1.2 Place 10 g of Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top.

7.1.3 Preelute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.1.4 Next, elute the column with 100 mL of 20% ethyl ether in hexane (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction. No solvent exchange is necessary. Adjust the volume of the cleaned-up extract to whatever volume is required (10 mL for Method 8060) and analyze by gas chromatography. Compounds that elute in this fraction are:

Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate

7.2 Nitrosamines:

7.2.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.2.2 Place 22 g of activated Florisil into a 20-mm I.D. chromatographic column. Tap the column to settle the Florisil and add about 5 mm of anhydrous sodium sulfate to the top.

7.2.3 Preelute the column with 40 mL of ethyl ether/pentane (15:85) (v/v). Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

7.2.4 Elute the column with 90 mL of ethyl ether/pentane (15:85) (v/v) and discard the eluate. This fraction will contain the diphenylamine, if it is present in the extract.

7.2.5 Next, elute the column with 100 mL of acetone/ethyl ether (5:95) (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction will contain all of the nitrosamines listed in the scope of the method.

7.2.6 Add 15 mL of methanol to the collected fraction, concentrate using pentane to prewet the K-D column and set the water bath at 70 to 75°C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of pentane. Analyze by gas chromatography.

7.3 Organochlorine pesticides, haloethers, and organophosphorous pesticides (see Tables 1 and 2 for fractionation patterns of compounds tested):

7.3.1 Reduce the sample extract volume to 10 mL prior to cleanup. The extract solvent must be hexane.

7.3.2 Add a weight of Florisil (nominally 20 g), predetermined by calibration, to a 20-mm I.D. chromatographic column. Settle the Florisil by tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep. Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

7.3.3 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1-2 mL hexane, adding each rinse to the column.

7.3.4 Place a 500-mL K-D flask and clean concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% ethyl ether in hexane (v/v) (Fraction 1) using a drip rate of about 5 mL/min. All of the haloethers are in this fraction. Remove the K-D flask and set aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (v/v) (Fraction 2), into a second K-D flask. Perform a third elution using 200 mL of 50% ethyl ether in hexane (v/v) (Fraction 3), and a final elution with 200 mL of 100% ethyl ether (Fraction 4), into separate K-D flasks.

7.3.5 Concentrate the eluates by standard K-D techniques using the water bath at about 85°C (75°C for Fraction 4). Adjust the final volume to whatever volume is required (1-10 mL). Analyze by gas chromatography.

7.4 Nitroaromatics and isophorone:

7.4.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.4.2 Prepare a slurry of 10 g activated Florisil in methylene chloride/hexane (1:9) (v/v) and place the Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top. Adjust the elution rate to about 2 mL/min.

7.4.3 Just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 30 mL of methylene chloride/hexane (1:9) (v/v) and continue the elution of the column. Discard the eluate.

7.4.4 Next, elute the column with 30 mL of acetone/methylene chloride (1:9) (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction, while exchanging the solvent to hexane. To exchange the solvent, reduce the elution solvent to about 10 mL. Add 50 mL of hexane, a fresh boiling chip, and return the reassembled K-D apparatus to the hot water bath. Adjust the

TABLE 1

DISTRIBUTION OF CHLORINATED PESTICIDES, PCBs, AND HALOETHERS INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery by Fraction[a]		
	1	2	3
Aldrin	100		
α-BHC	100		
β-BHC	97		
δ-BHC	98		
γ-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Ensosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Haloethers	R		
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

[a]Eluant composition: Fraction 1 - 6% ethyl ether in hexane
Fraction 2 - 15% ethyl ether in hexane
Fraction 3 - 50% ethyl ether in hexane

R = Recovered (no percent recovery data presented).

SOURCE: U.S. EPA and FDA data.

TABLE 2

DISTRIBUTION OF ORGANOPHOSPHOROUS PESTICIDES
INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery by Fraction[a]			
	1	2	3	4
Azinophos methyl			20	80
Bolstar (Sulprofos)	ND	ND	ND	ND
Chlorpyrifos	>80			
Coumaphos	NR	NR	NR	
Demeton	100			
Diazinon		100		
Dichlorvos	NR	NR	NR	
Dimethoate	ND	ND	ND	ND
Disulfoton	25-40			
EPN		>80		
Ethoprop	V	V	V	
Fensulfothion	ND	ND	ND	ND
Fenthion	R	R		
Malathion		5	95	
Merphos	V	V	V	
Mevinphos	ND	ND	ND	ND
Monochrotophos	ND	ND	ND	ND
Naled	NR	NR	NR	
Parathion		100		
Parathion methyl		100		
Phorate	0-62			
Ronnel	>80			
Stirophos (Tetrachlorvinphos)	ND	ND	ND	ND
Sulfotepp	V	V		
TEPP	ND	ND	ND	ND
Tokuthion (Prothiofos)	>80			
Trichloronate	>80			

[a]Eluant composition: Fraction 1 - 200 mL of 6% ethyl ether in hexane
Fraction 2 - 200 mL of 15% ethyl ether in hexane
Fraction 3 - 200 mL of 50% ethyl ether in hexane
Fraction 4 - 200 mL of 100% ethyl ether

R = Recovered (no percent recovery information presented) (U.S. FDA).
NR = Not recovered (U.S. FDA).
V = Variable recovery (U.S. FDA).
ND = Not determined.

SOURCE: U.S. EPA and FDA data.

final volume of the cleaned-up extract to whatever volume is required (1-10 mL). Compounds that elute in this fraction are:

2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone
Nitrobenzene.

Analyze by gas chromatography.

7.5 Chlorinated hydrocarbons:

7.5.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.5.2 Place 12 g of Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of anhydrous sodium sulfate to the top.

7.5.3 Preelute the column with 100 mL of petroleum ether. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract to the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 200 mL of petroleum ether and collect the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction should contain all of the chlorinated hydrocarbons:

2-Chloronaphthalene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
1,2,4-Trichlorobenzene.

7.5.4 Concentrate the fraction, using hexane to prewet the column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the final volume of the cleaned-up extract to whatever volume is required (1-10 mL). Analyze by gas chromatography.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the distribution of chlorinated pesticides, PCB's, and haloethers in various Florisil column fractions.

9.2 Table 2 indicates the distribution of organophosphorous pesticides in various Florisil column fractions.

10.0 REFERENCES

1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. Floridin of ITT System, Florisil: Properties, Application, Bibliography, Pittsburgh, Pennsylvania, 5M381DW.

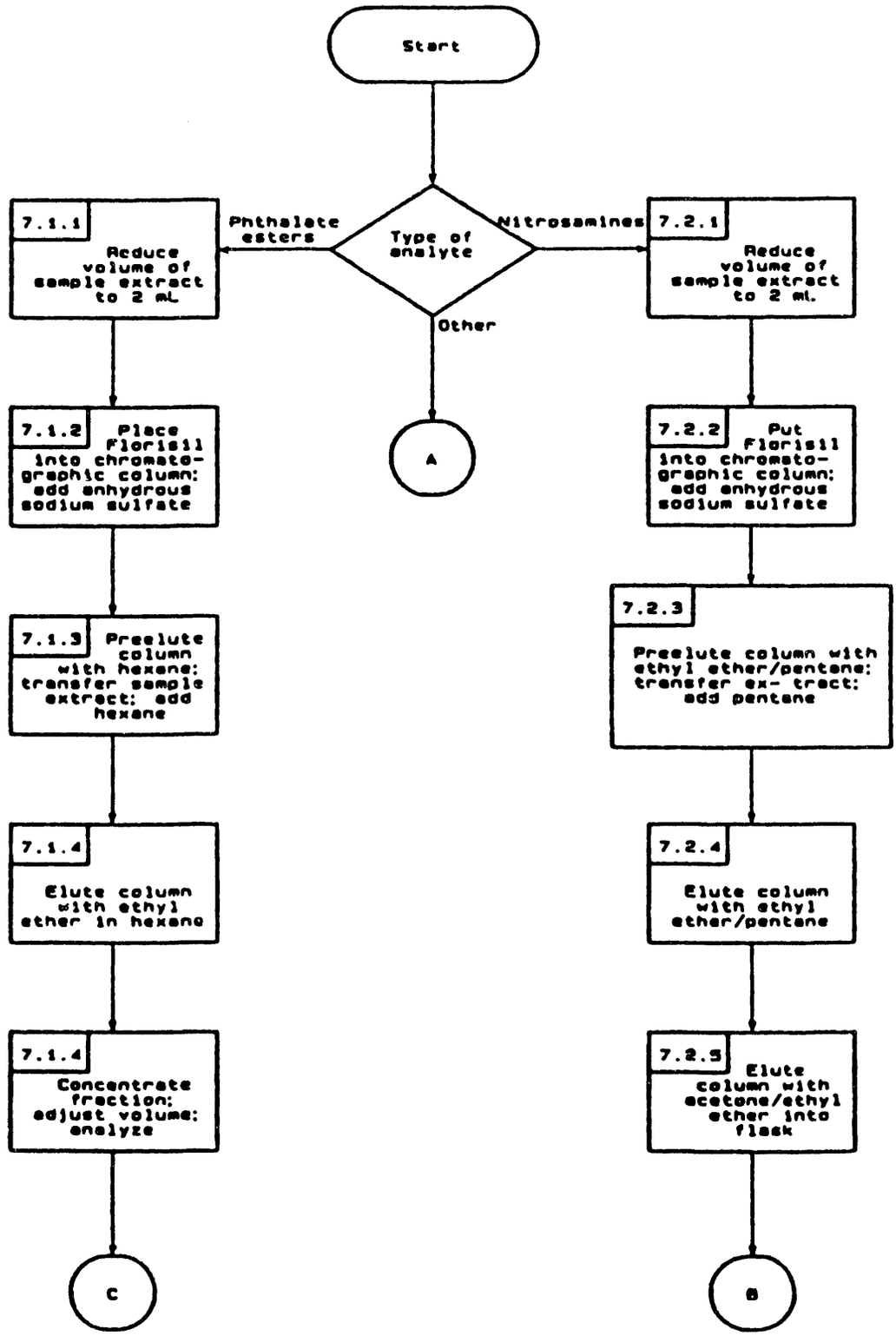
3. Mills, P.A., "Variation of Florisil Activity; Simple Method for Measuring Absorbent Capacity and its use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29, 1968.

4. U.S. Food and Drug Association, Pesticides Analytical Manual (Volume 1), July 1985.

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

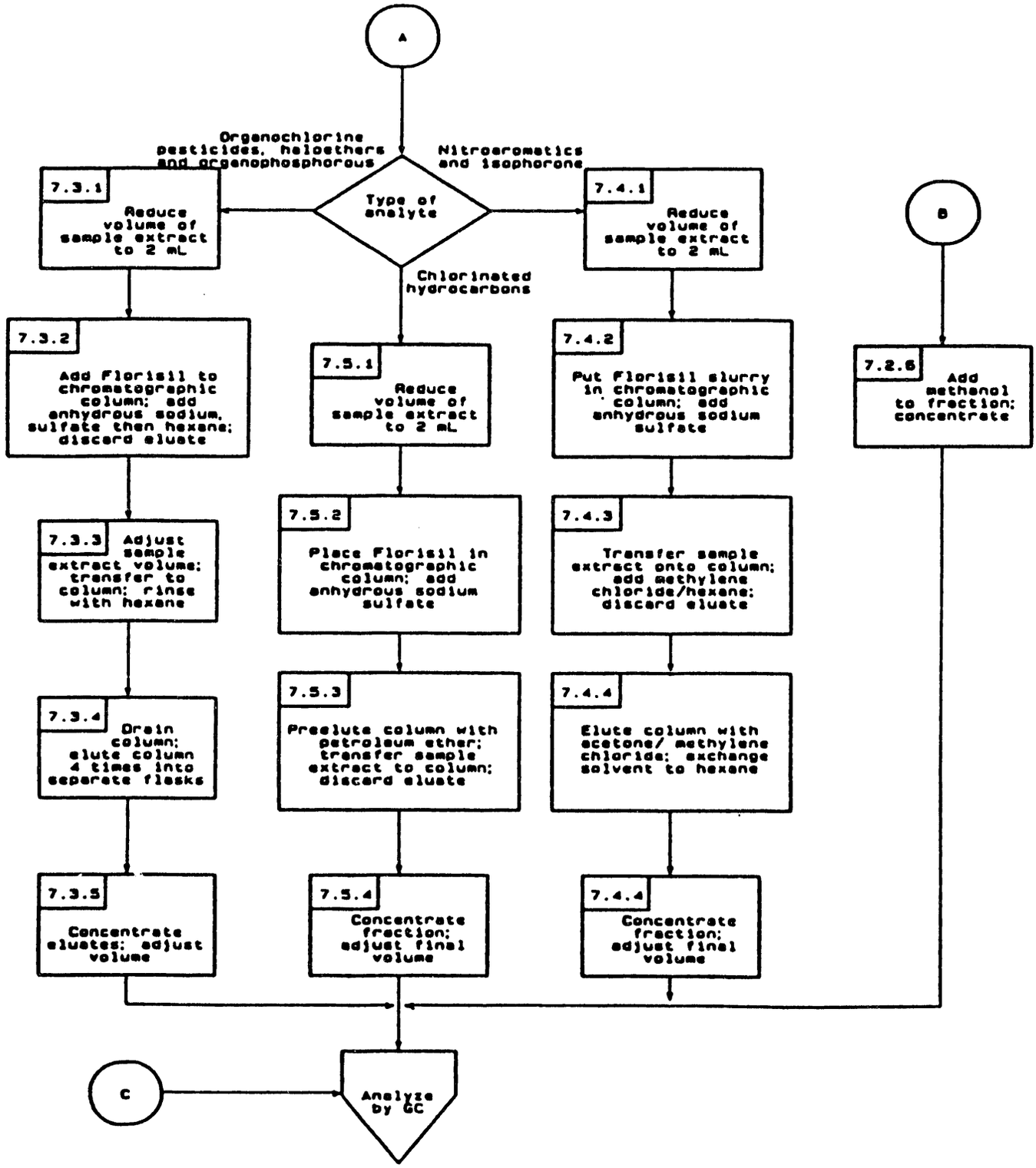
METHOD 3620

FLORISIL COLUMN CLEANUP



METHOD 3620

FLORISIL COLUMN CLEANUP
(Continued)



PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-361, SILICA GEL CLEANUP OF SAMPLES FOR DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS

APPLICABILITY

This procedure applies to the cleanup of samples by silica gel column chromatography for the determination of semivolatile organic compounds . It is used to provide cleanup separations based on the polarity of the sample constituents.

DEFINITIONS

None

RESPONSIBLE STAFF

- Cognizant scientist
- Analyst

PROCEDURE

See Attachment 1 for the detailed procedure. This procedure is the USEPA SW-846 Method 3630.

QUALITY CONTROL

See attachment 1 of Method PNL-ALO-120 for sample preparation in the GC/MS method for semivolatiles, Method PNL-ALO-345 for the GC/MS analysis for semivolatile organic compounds, and in the quality control sections of other sample preparation and analysis procedures as appropriate. The use of the silica gel cleanup may affect the surrogate and matrix spike recoveries.

REFERENCES

USEPA Test Methods for Evaluating Solid Wastes, SW-846, Volume IB, Method 3630 and Chapter 1, November, 1986.

PNL-ALO-120, Extraction of Single Shell Tank Samples for the Analysis of Semivolatile Organic Compounds.

PNL-ALO-345, GC/MS Analysis of Extractable Semivolatile Organic Compounds. USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Multi-media, Multi-concentration, 2/88.

Author	Date	Project Mgr.	Date	QAD Representative	Date
[signature]	1-30-91	[signature]	1-30-91	[signature]	1/31/91
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
[signature]	1-30-91	[signature]	1/30/91		

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PNL-ALO-361	0	APR 2 6 1991	1	1

METHOD 3630

SILICA GEL CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is for separating the analytes from interfering compounds of a different chemical polarity.

1.2 General applications (Gordon and Ford):

1.2.1 **Activated:** Heated at 150-160°C for several hours.
USES: Separation of hydrocarbons.

1.2.2 **Deactivated:** Containing 10-20% water. USES: An adsorbent for most functionalities with ionic or nonionic characteristics, including alkaloids, sugar esters, glycosides, dyes, alkali metal cations, lipids, glycerides, steroids, terpenoids and plasticizers. The disadvantages of deactivated silica gel are that the solvents methanol and ethanol decrease adsorbent activity.

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing polynuclear aromatic hydrocarbons and derivatized phenolic compounds.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Chromatographic column: 250-mm long x 10-mm I.D.; with Pyrex glass wool at bottom and a Teflon stopcock.
NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits

may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers: 500-mL.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Muffle furnace.

4.5 Reagent bottle: 500-mL.

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.8 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

5.1 Silica gel: 100/200 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr at 130°C in a shallow glass tray, loosely covered with foil.

5.2 Sodium sulfate (ACS): Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.3 Eluting solvents: Cyclohexane, hexane, 2-propanol, toluene, methylene chloride, pentane (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Polynuclear aromatic hydrocarbons:

7.1.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. Add 1 to 10 mL of the sample extract (in methylene chloride) and a boiling chip to a clean K-D concentrator tube. Add 4 mL of cyclohexane and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride to the top. Place the micro-K-D apparatus on a boiling (100°C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 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 the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of cyclohexane. Adjust the extract volume to about 2 mL.

7.1.2 Prepare a slurry of 10 g of activated silica gel in methylene chloride and place this into a 10-mm I.D. chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

7.1.3 Preelute the column with 40 mL of pentane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane eluate.

7.1.4 Next, elute the column with 25 mL of methylene chloride/-pentane (2:3)(v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction to whatever volume is required (1-10 mL). Proceed with HPLC or GC analysis. Components that elute in this fraction are:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(ghi)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene

Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

7.2 Derivatized phenols:

7.2.1 This silica gel cleanup procedure is performed on sample extracts that have undergone pentafluorobenzyl bromide derivatization as described in Method 8040.

7.2.2 Place 4.0 g of activated silica gel into a 10-mm I.D. chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top of the silica gel.

7.2.3 Preelute the column with 6 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, pipet onto the column 2 mL of the hexane solution that contains the derivatized sample or standard. Elute the column with 10.0 mL of hexane and discard the eluate.

7.2.4 Elute the column, in order, with: 10.0 mL of 15% toluene in hexane (Fraction 1); 10.0 mL of 40% toluene in hexane (Fraction 2); 10.0 mL of 75% toluene in hexane (Fraction 3); and 10.0 mL of 15% 2-propanol in toluene (Fraction 4). All elution mixtures are prepared on a volume:volume basis. Elution patterns for the phenolic derivatives are shown in Table 1. Fractions may be combined, as desired, depending upon the specific phenols of interest or level of interferences. Proceed with GC analysis (Method 8040).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides performance information on the fractionation of phenolic derivatives using this method.

10.0 REFERENCES

1. Gordon, A.J., and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References, (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

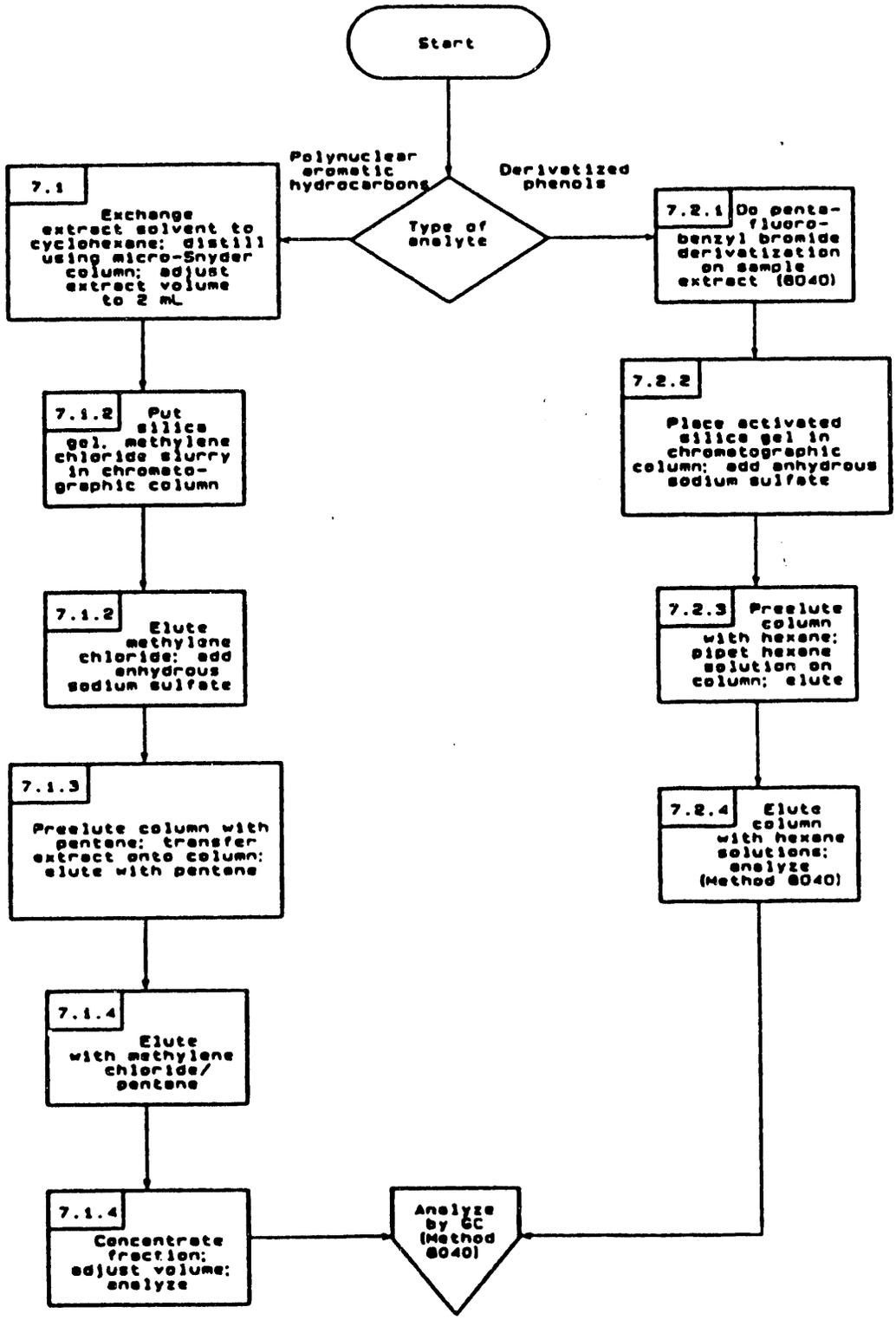
TABLE 1. SILICA GEL FRACTIONATION OF PFBB DERIVATIVES

Parameter	Percent Recovery by Fraction[1]			
	1	2	3	4
2-Chlorophenol		90	1	
2-Nitrophenol			9	90
Phenol		90	10	
2,4-Dimethylphenol		95	7	
2,4-Dichlorophenol		95	1	
2,4,6-Trichlorophenol	50	50		
4-Chloro-3-methylphenol		84	14	
Pentachlorophenol	75	20		
4-Nitrophenol			1	90

[1] Eluant composition:

Fraction 1-15% toluene in hexane.
Fraction 2-40% toluene in hexane.
Fraction 3-75% toluene in hexane.
Fraction 4-15% 2-propanol in toluene.

METHOD 3630
SILICA GEL CLEANUP



PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-362, ACID-BASE PARTITION CLEANUP OF SAMPLES FOR SEMIVOLATILE ORGANICS ANALYSIS

APPLICABILITY

This procedure applies to the cleanup of samples for the determination of semivolatile organic compounds. The procedure involves extraction of the acidic compounds from the organic solvent into a basic solution leaving the base/neutral compounds in the organic phase. The aqueous fraction is acidified, and then extracted with an organic solvent. The two phases are concentrated and analyzed, or if needed, additional cleanup can be applied to either or both of these phases prior to the analysis. This procedure is particularly useful for cleanup of samples with respect to alkanes.

DEFINITIONS

None

RESPONSIBLE STAFF

- Cognizant scientist
- Analyst

PROCEDURE

See Attachment 1 for the detailed procedure. This procedure is the USEPA SW-846 Method 3650 (Revision 1, December, 1987).

QUALITY CONTROL

See PNL-ALO-120 for sample preparation in the GC/MS analysis for semivolatile organics, Method PNL-ALO-345 for the GC/MS analysis for semivolatile organic compounds, and in the quality control sections of other sample preparation and analysis procedures as appropriate. The partitioning operations in this cleanup procedure may affect the surrogate and matrix spike recoveries.

REFERENCES

USEPA Test Methods for Evaluating Solid Wastes, Volume IB, Method 3650 and Chapter 1, Revision 1, December 1987.

Author	Date	Project Mgr.	Date	QAD Representative	Date
	1-30-91		1-30-91		4/31/91
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
	1-30-91		1/30/91		

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PNL-ALO-120, Extraction of Single Shell Tank Samples for the Analysis of Semivolatile Organic Compounds.

PNL-ALO-345, GC/MS Analysis of Extractable Semivolatile Organic Compounds, and USEPA Contract Laboratory Program Statement of work for Organic Analysis, Multi-media, Multi-concentration, 2/88.

METHOD 3650

ACID-BASE PARTITION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3650 was formerly Method 3530 in the second edition of this manual.

1.2 This is a liquid-liquid partitioning cleanup method to separate acid analytes, e.g. organic acids and phenols, from base/neutral analytes, e.g. amines, aromatic hydrocarbons, and halogenated organic compounds, using pH adjustment. It may be used for cleanup of petroleum waste prior to alumina cleanup. Specific examples of compounds that are separated by this method are in Table 1.

2.0 SUMMARY OF METHOD

2.1 The solvent extract from a prior solvent extraction method is shaken with water that is strongly basic. The acid analytes partition into the aqueous layer, whereas, the basic and neutral compounds stay in the organic solvent. The base/neutral fraction is concentrated and is then ready for further cleanup, if necessary, or analysis. The aqueous layer is acidified and extracted with an organic solvent. This extract is concentrated and is then ready for analysis of the acid analytes.

3.0 INTERFERENCES

3.1 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.2 A method blank must be run for the compounds of interest prior to use of the method. The interferences must be below the method detection limit before this method is applied to actual samples.

4.0 APPARATUS AND MATERIALS

4.1 Drying column - 20 mm i.d. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to clean after highly contaminated extracts have been passed through them. Columns without frits are recommended. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent (Table 1) prior to packing the column with adsorbent.

4.2 Kuderna-Danish (K-D) apparatus (Kontes K-570025-0500)

4.2.1 Concentrator tube - 10-mL graduated (Kontes K570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of the extracts.

4.2.2 Evaporation flask - 500-mL (K-570001-0500 or equivalent). Attach to concentrator tube with springs.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Vials - Glass, 2-mL capacity with Teflon lined screw-cap.

4.4 Water bath - Heated, concentric ring cover, temperature control of ± 2°C. Use this bath in a hood.

4.5 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 pH indicator paper - pH range including the desired extraction pH.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.4 Sodium hydroxide (10N), NaOH. Dissolve 40 g of sodium hydroxide in 100 mL of water.

5.5 Sulfuric acid (1:1 v/v in water), H_2SO_4. Slowly add 50 mL H_2SO_4 to 50 mL of water.

5.6 Sodium sulfate, Na_2SO_4. Granular, anhydrous, purify by rinsing with acetone followed by the elution solvent and then drying at 200°C for 4 hours.

5.7 Acetone, CH_3COCH_3. Pesticide quality or equivalent.

5.8 Methanol, CH_3OH. Pesticide quality or equivalent.

5.9 Ethyl ether, $C_2H_5OC_2H_5$. Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

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

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

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

7.4 Seal and shake the separatory funnel for at least 2 minutes with periodic venting to release excess pressure.

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

7.5 Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques 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.

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

7.7 Water soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes are only in the aqueous phase, discard the methylene chloride and proceed to Step 7.8. If the analytes are only in the methylene chloride, discard the aqueous phase and proceed to Step 7.10.

7.8 Externally cool the 125-mL Erlenmeyer flask with ice while adjusting the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Transfer the cool aqueous phase to a clean 125-mL separatory funnel. Add 20 mL of methylene chloride to the separatory funnel and shake for at least 2 minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask.

7.9 Add 20-mL of methylene chloride to the separatory funnel and extract at pH 1-2 a second time. Perform a third extraction in the same manner combining the extracts in the Erlenmeyer flask.

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

7.11 Dry both acid and base/neutral fractions by passing them through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried fractions in K-D concentrators. Rinse the Erlenmeyer flasks which contained the solvents and the columns with 20 mL of methylene chloride to complete the quantitative transfer.

7.12 Concentrate both acid and base/neutral fractions as follows: Add one or two boiling chips to the flask and attach a three ball macro-Snyder column. Prewet 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 warm water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to cool. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride.

7.13 Add another one or two boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the volume of the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to cool. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1 mL with methylene chloride.

7.14 The acid fraction is now ready for analysis. If the base/neutral fraction requires further cleanup by the alumina column cleanup for petroleum waste (Method 3611), the solvent may have to be changed to hexane. To the 1 mL base/neutral fraction, 5 mL of hexane should be added, and this mixture concentrated to 1 mL using the micro K-D apparatus (repeat 2 more times). If no further cleanup of the base/neutral extract is required, it is also ready for analysis.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for general quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For samples that are cleaned using this method, the associated quality control samples must be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed.; U.S. Environmental Protection Agency. Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1987; SW-846; 955-001-00000-1.

2. Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1982; EPA-600/4-82-057.

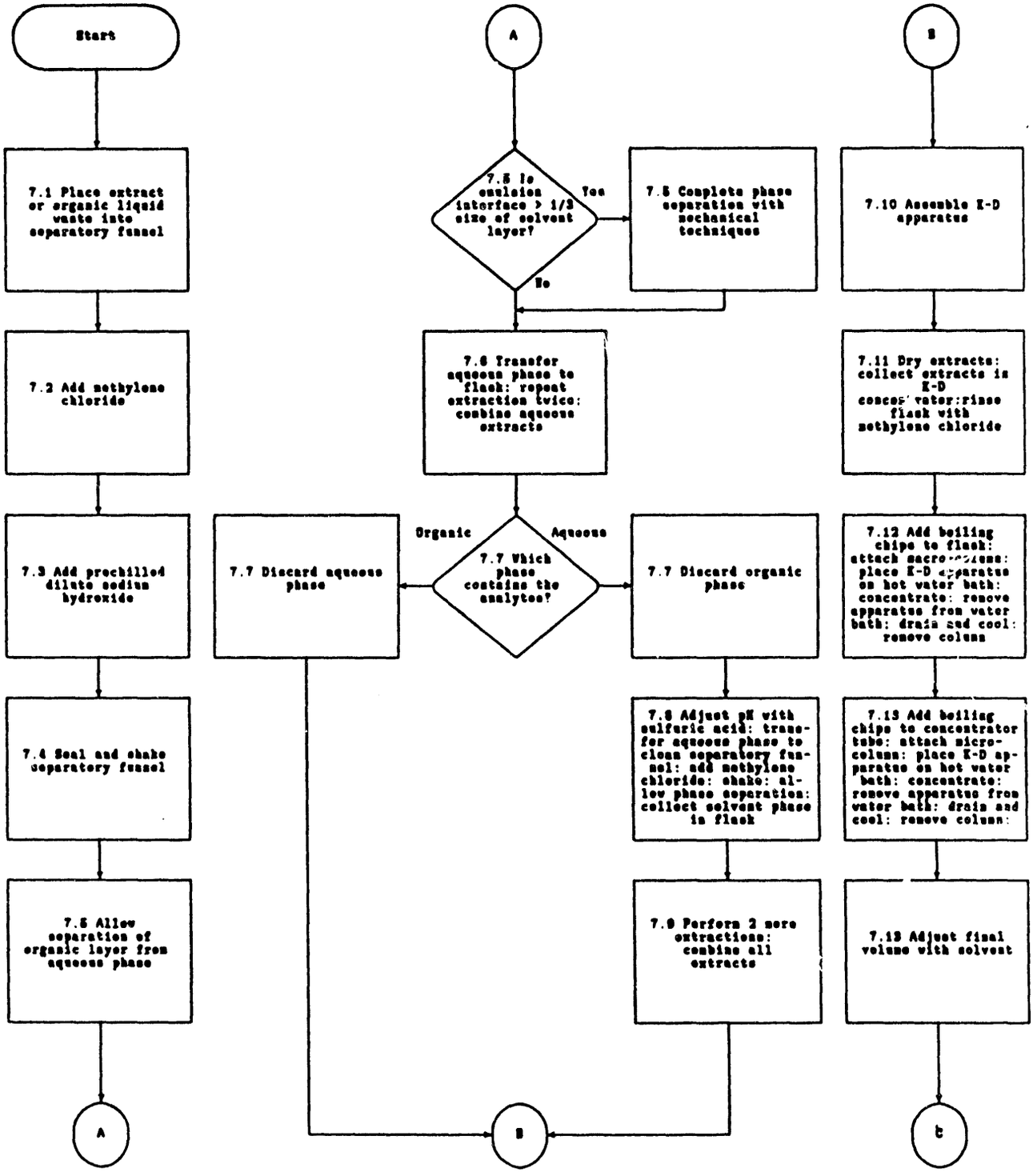
3. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

4. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ATSM: Philadelphia, PA, 1985; D1193-77.

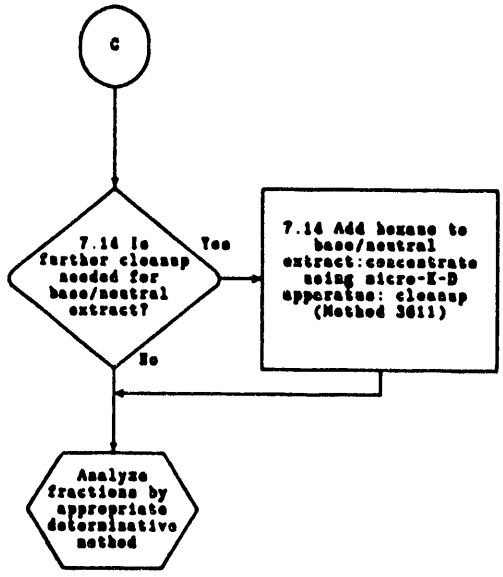
TABLE 1.
ANALYTES WHICH CAN BE PARTITIONED BY METHOD 3650

Compound	Chemical Abstracts Service Registry Number	Fraction
Benz(a)anthracene	56-55-3	Base-neutral
Benzo(a)pyrene	50-32-8	Base-neutral
Benzo(b)fluoranthene	205-99-2	Base-neutral
Chlordane	57-74-9	Base-neutral
Chlorinated dibenzodioxins		Base-neutral
2-Chlorophenol	95-57-8	Acid
Chrysene	218-01-9	Base-neutral
Creosote	8001-58-9	Base-neutral and Acid
Cresol(s)		Acid
Cresylic acid(s)		Acid
Dichlorobenzene(s)		Base-neutral
Dichlorophenoxyacetic acid	94-75-7	Acid
2,4-Dimethylphenol	105-67-9	Acid
Dinitrobenzene	25154-54-5	Base-neutral
4,6-Dinitro-o-cresol	534-52-1	Acid
2,4-Dinitrotoluene	121-14-2	Base-neutral
Heptachlor	76-44-8	Base-neutral
Hexachlorobenzene	118-74-1	Base-neutral
Hexachlorobutadiene	87-68-3	Base-neutral
Hexachloroethane	67-72-1	Base-neutral
Hexachlorocyclopentadiene	77-47-4	Base-neutral
Naphthalene	91-20-3	Base-neutral
Nitrobenzene	98-95-3	Base-neutral
4-Nitrophenol	100-02-7	Acid
Pentachlorophenol	87-86-5	Acid
Phenol	108-95-2	Acid
Phorate	298-02-2	Base-neutral
2-Picoline	109-06-8	Base-neutral
Pyridine	110-86-1	Base-neutral
Tetrachlorobenzene(s)		Base-neutral
Tetrachlorophenol(s)		Acid
Toxaphene	8001-35-2	Base-neutral
Trichlorophenol(s)		Acid
2,4,5-TP (Silvex)	93-72-1	Acid

METHOD 3650
ACID-BASE PARTITION CLEANUP



METHOD 3650
(Continued)



PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-363, CONCENTRATED ACID WASH CLEANUP

APPLICABILITY

This procedure is a modification of the acid cleanup portion of the EPA Test Method, "The Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils", EPA-600/4-81-045, September 1982. This procedure may be utilized on extracted residues produced by the method "Sample Preparation for Pesticide/PCB Analysis in Water and Soil/Sediment", PNL-ALO-347, after the specified method cleanup procedures have proven inadequate or in cases where the pesticides are not target analytes. Additionally, this method may be used for other analytes that are able to withstand this rigorous cleanup procedure such as selected dioxins or polynuclear aromatics. It may be used on any matrix or extracted residues where the contaminants of concern are susceptible to concentrated acid wash and the analytes are proven to provide good recovery.

DEFINITIONS

PCBs (Polychlorinated Biphenyls)
Aroclor (Commercial mixtures of PCBs)

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 This method is an acid wash of extracted sample residues that have not responded favorably to gel permeation chromatography or alumina column cleanup as specified in the procedure "Sample Preparation for Pesticide/PCB Analysis in Water and Soil/Sediment", PNL-ALO-347 and subsequent analysis by "Analysis for Pesticide/PCBs by Gas Chromatography with Electron Capture Detection", PNL-ALO-346. This cleanup should be used with caution as it destroys the individual pesticide

Author	Date	Project Mgr.	Date	QAD Representative	Date
	2-12-91	B.M. Gillespie	2-12-91		2/12/91
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
	2-12-91		2/12/91		

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analytes and forfeits the ability to monitor the surrogate compound dibutylchlorendate (DBC) specified in the Pesticide/PCB analysis method.

1.2 This method may be used for cleanup of waste oils prior to analysis for PCBs. It is highly recommended that an alternate surrogate compound(s) be chosen other than DBC such as those recommended in EPA-CLP SOW 3/90 or SW-846 method 8080.

2.0 SUMMARY OF METHOD

2.1 An aliquot of previously extracted residue that has been exchanged into hexane or an oil sample is transferred to a screw-cap test tube. Concentrated sulfuric acid is added and the tube is agitated using a vortex mixer. After adequate phase separation, the hexane layer is drawn off and analyzed.

3.0 INTERFERENCES

3.1 Sample residues that contain high boiling hydrocarbons co-eluting on the chromatographic system with the PCBs will cause quenching of the electron capture detector (ECD) specified for use in Pesticide/PCB Analysis, PNL-ALO-346. The quenching of the ECD can produce results that are as much as 10-20% lower than the true value if none of the hydrocarbon was removed in the acid cleaning step. This may also affect the final residue volume if large amounts of oil remain. Monitoring the final residue volume after cleanup and reviewing the chromatograms for negative response are means available to evaluate the presence of interferences. Spike and duplicate spike samples will also provide a quantitative assessment of this effect.

3.2 Chlorinated solvents respond well on the ECD. It is imperative that sample residues extracted using methylene chloride are fully exchanged into hexane prior to performing the acid wash and subsequent analysis. Residues should be tightly capped as soon as possible to avoid adsorption of chlorinated solvent vapors. Small quantities of methylene chloride in the residue can effect the response of the ECD. The resulting error can be high or low depending on the quantity of methylene chloride, analyte, and the analyte retention time.

4.0 APPARATUS AND MATERIALS

4.1 Balance: Analytical, capable of accurately weighing 0.01 gram.

4.2 Vials: 1.5-mL amber screw top with teflon lined closures.

4.3 Pipets: Pasteur type, 9 inch.

4.4 Culture Tube: disposable 16 x 150 mm, screw top with teflon closures.

4.5 Centrifuge: Bench top with openings capable of holding 16 x 150 culture tubes and achieving 2000 rpm.

4.6 Volumetric Pipets: Disposable glass serological, 1.0 and 5.0 mL. A repipetor capable of delivering sulfuric acid may be substituted for the 5.0 mL volumetric pipet if desired.

5.0 REAGENTS

5.1 Hexane: Pesticide grade or equivalent.

5.2 Sulfuric Acid: A.C.S. or equivalent.

5.3 Commercially prepared standards may be used if the appropriate certification of concentration is obtained. For spike solutions, a single aroclor at the appropriate concentration (typically 10 ug/mL) may be purchased or obtained by dilution of certified stock or neat materials. Surrogate compounds such as 2,3,4,5-tetrachloroxylene and decachlorobiphenyl may be obtained in the same manner with typical concentrations usable for this method being 1.0-2.0 ug/mL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples from residues to be subjected to this cleaning shall follow guidelines provided for in the appropriate procedure, such as PNL-ALO-347.

6.2 Sample bottles for oil samples shall be pre-cleaned amber glass with teflon lined closures. Oil samples shall be stored in a cool, dry, dark location. Sample storage times shall not exceed 28 days.

7.0 PROCEDURE

7.1 The following residue or sample quantities may be modified to suit the application. Care should be taken to keep track of the modifications effect on the final dilution factor used for quantitation.

7.2 Residue Preparation:

7.2.1 Pipet 5 mL of concentrated sulfuric acid into a 16 x 150 mm screw top culture tube.

7.2.2 Pipet a 1.0 mL aliquot of sample extract residue that has been exchanged into hexane to the tube containing sulfuric acid. Mark the tube at the bottom and top of the hexane layer.

7.2.3 Repeat steps 7.2.1 and 7.2.2 for the blank residue. Include the spike, spike duplicate and the un-spiked sample.

7.2.4 Seal the culture tube using a teflon lined screw-cap and shake or vortex briefly. Slowly loosen the cap to relieve pressure and then re-seal.

7.2.5 Shake or vortex the tube for one minute. The sulfuric acid phase should turn yellow or darken.

7.2.6 Loosen the cap slightly and allow the mixture to stand until the phases have fully separated, usually several minutes.

7.2.7 Centrifuge the sample for 3-5 minutes at approximately 2000 rpm if adequate separation is not observed after standing.

7.2.8 Mark the tube again at the bottom and top of the hexane layer. Note the recovery of this layer on the bench sheet if approximately 100% recovery is not obtained.

7.2.9 Transfer the hexane layer to a 1.5 mL amber vial. Withdraw the hexane well above the acid layer taking care not to entrain any of the acid.

7.2.10 If the sample is highly contaminated, a second or third acid cleanup may be required.

7.2.11 Analyze the sample according to the appropriate procedure.

7.3 Sample Preparation:

7.3.1 Weigh into a culture tube approximately 1 gram of waste oil sample. Record the weight to the nearest 0.01 grams. A 150 mL beaker may be used to hold the tube upright on the balance if needed.

7.3.2 If surrogate(s) are used (highly recommended), add them to all of the samples at the appropriate concentration contained in hexane. For tetrachloroxylene or decachlorobiphenyl, final residue concentrations of 100-200 ng/mL are typical.

7.3.4 Add to the tube designated for spike and spike duplicate the appropriate spike compound in hexane. For the analysis of PCBs, the residue final concentration should typically be 1.0 ug/mL.

7.3.4 Add an appropriate volume of hexane so that the total volume of hexane added to the sample is constant including the portion contributed by the surrogate and spike addition. Typically final volumes range from 1 to 10 mL.

7.3.5 Pipet 5 mL of concentrated sulfuric acid into each of the tubes containing samples.

7.3.6 Proceed with steps 7.2.4 through 7.2.11. For PCB analysis proceed with procedure PNL-ALO-346.

8.0 QUALITY CONTROL

8.1 Before processing samples, the analyst shall demonstrate through the analysis of a method blank that all glassware and reagents are interference free. With each batch of samples, or whenever there is a change in reagents, a method blank shall be processed as a safeguard against chronic laboratory contamination. The blank samples must be carried through all stages of the sample preparation.

8.2 Standard quality assurance practices shall be employed while using this method. Fortified samples shall be carried through all stages of sample preparation and analyzed to validate sensitivity and accuracy of the analysis.

8.3 Quality control limits for recovery of spiked aroclors or the surrogates tetrachloroxylene and decachlororbiphenyl have not been established by the EPA. Recovery of these compounds should be monitored by use of the EPA advisory limits of 20-150%. These limits are only advisory and no further action by the laboratory is required if these limits are exceeded. Persistent failure to meet these limits warrant investigation into applicable test parameters such as re-validation of standard solutions and other pertinent variables.

8.4 Tolerances for all values given within this method are to within the first, non-zero, significant integer, including the number 10, that is specified. For example, 5 mL implies accuracy to within +/- 1 mL, while 5.0 mL implies accuracy to within +/- 0.1 mL. If 100 mL is specified, it implies accuracy to +/- 10 mL.

9.0 METHOD PERFORMANCE AND SPECIFIC QUALIFICATION

9.1 This cleanup method was tested over a six month period by the EPA using the electron capture detector. Care was taken to exclude any samples that formed an emulsion with the acid. The sample was withdrawn well above the acid phase. Under these conditions, no adverse effects associated with column performance and detector sensitivity to PCBs was noted.

9.2 The EPA has determined through replicate analyses of 7-14 samples employing several aroclors that an MDL of 1 mg/kg is reasonable for waste oil samples. Analysis of spiked waste oils at PNL has found an MDL of 0.1 to 0.4, depending on the aroclor, is quite reasonable. The difference is most likely attributable to the EPA employing packed column methods
rather than the higher resolution provided by capillary column in analysis method PNL-ALO-346. Either method provides limits lower than currently required by the regulatory detection needs at this time.

9.3 This procedure is self qualifying due to dependence on analytical standards. It is qualified additionally through quality control samples and by Independent Technical Review.

REFERENCES

1. Bellar, T. A. and Lichtenberg, J. L., Test Method, The Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils, United States Environmental Protection Agency, EPA-600/4-81-045, September 1982.

2. Organochlorine Pesticides and PCBs, SW-846, Method 8080, Test Methods for Evaluating Solid Waste, Third Edition, United States Environmental Protection Agency, November 1986.

3. Sample Preparation for Pesticide/PCB Analysis in Water and Soil/Sediment, PNL-ALO-347.

4. Analysis for Pesticide/PCBs by Gas Chromatography with Electron Capture Detection, PNL-ALO-346.

5. Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, USEPA Contract Laboratory Program, Document Number OLM01.0, March 1990.

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-380.2 R0
Page 1 of 1

A.

Document Number: PNL-ALO-380 **Revision Number:** 0

Document Title: DETERMINATION OF CARBON IN SOLIDS USING THE COULOMETRICS CARBON DIOXIDE COULOMETER

Document's Original Author: DL Baldwin

Effective Date of ICN: 03/06/92

Change Requested by: WT Cobb

B. **Action:**

1) Replace all pages (Due to new format).

C. **Effect of Change:**

1) To update and clarify procedure.

2) Outlines specific standard recovery range.

D. **Reason for Change/Description of Change:**

1) Reason: Filled, but untitrated, titration cell must be inserted into the cell holder before the initial systems check can be performed.

Description: See changes in redline and strike out in section 4.12.7.

2) Reason: Specifies standard recovery range.

Description: See changes in redline in section 4.2.1.

E. **Approval Signatures:**
(Please sign and date)

Type of Change: (Check one):

X Minor ___ Major

Process Quality Department: TL Ehlert TL Ehlert **Date:** 3/12/92

Approval Authority: AG King A.G. King **Date:** 3/12/92

Other Approvals: BM Gillespie B.M. Gillespie **Date:** 3/12/92

: _____ **Date:** / /

INTERIM CHANGE NOTICE
ICN

ICN-PNL-ALO-380.1 R0
PAGE 1 OF 1

A. Document Number: PNL-ALO-380 Revision Number: 0

Document Title: DETERMINATION OF CARBON IN SOLIDS USING THE COULOMETRICS CARBON DIOXIDE COULOMETER

Document's Original Author: DL BALDWIN

Effective Date of ICN: 12/20/91

Change Requested by: WT COBB

B. Action:

Replace all pages (1-7) with new pages (1-8)

C. Effect of Change:

1. To update & clarify procedure to include system check

D. Reason for Change/Description of Change:

Reason: To update and clarify procedure

Description: See changes in redline and strike out

E. Approval Signatures
(Please sign and Date)

Type of Change (Check (✓) one)
( )Minor Change (✓)Major Change

QS&R Department Concurrence: GK Gerke GK Gerke Date: 12/20/91

Approval Authority: AG King A. King Date: 12/20/9

Other Approvals: BM Gillespie B. M Gillespie Date: 12/20/91

: _____ Date: _____

TITLE: PNL-ALO-380: DETERMINATION OF CARBON IN SOLIDS USING THE COULOMETRICS CARBON DIOXIDE COULOMETER (replaces 7-40.37)

1.0 APPLICABILITY

This procedure can be used for determining total organic carbon and total carbon in solid samples.

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Analyst
Cognizant Scientist

4.0 PROCEDURE

4.1 Equipment and Materials

- Coulometrics Model 5011 CO_2 Coulometer
- Coulometrics Model 5020 Total Carbon Apparatus
- Coulometrics Model 5022 Ladle Components
- Analytical balance (capable of weight to 0.1 mg)
- Purified O_2
- Anhydrous magnesium perchlorate
- Acid Dichromate on silocel (from vendor)
- Manganese dioxide
- 45% KOH (wt/vol)
- Barium Chromate
- Reduced Silver
- Quartz wool
- Potassium Iodide
- Coulometer Cathode Solution (proprietary)
- Coulometer Anode Solution (proprietary)

4.2 Description of Procedure

Samples are combusted in an oxygen atmosphere to convert organic and inorganic forms of carbon to carbon dioxide (CO_2). The

Author / Date	Project Mgr. / Date	QAD Representative / Date
DL Baldwin	BM Gillespie	GK Gerke
Technical Reviewer / Date	Line Mgr. / Date	Other / Date
GA Ross	AG King 3/12/91	original signatures on file

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combustion temperature is selected (up to 1100°C) either to completely oxidize all carbon forms, or to selectively oxidize only the organic carbon components. The combustion product gases are swept through the barium chromate catalyst/scrubber to ensure complete oxidation of carbon to CO_2. Non-carbon combustion products such as SO_2, SO_3, HX and NO_x, are removed from the gas stream by a series of chemical scrubbers. The CO_2 is then measured with the CO_2 coulometer.

The coulometer cell is filled with a proprietary solution containing monoethanolamine and a colorimetric indicator. A platinum cathode and a silver anode are positioned in the cell and the assembly is positioned between a light source and a photodetector in the coulometer.

When a gas stream passes through the solution, CO_2 is quantitatively absorbed, reacting with monoethanolamine to form a titratable acid (hydroxyethylcarbamic acid). This acid causes the color indicator to fade. Photodetection monitors the change in the solution's color as percent trasmittance (%T). As the %T increases, the titration current is automatically activated to stoichiometrically generate base at a rate proportional to the %T. When the solution returns to its original color (original %T), the current stops.

The titration current is continally measured and integrated to operator selected units on the digital display.

A summary of the chemical reactions occurring in the coulometer cell is given below.

$$\underset{\text{monoethanolamine}}{CO_2 + HOCH_2CH_2NH_2} \longrightarrow \underset{\text{hydroxyethylcarbamic acid}}{HOCH_2CH_2NHCOOH}$$

$$I^- + Ag^o \longrightarrow AGI(s) + e^-$$

$$2\ H_2O + 2e^- \longrightarrow H_2\ (g) + 2\ OH^-$$

$$HOCH_2CH_2NHCOOH + OH^- \longrightarrow HOCH_2CH_2NHCOO^- + H_2O$$

4.2.1 Initial Systems Check

NOTE: Filled, but untitrated, titration cell must be inserted into the cell holder before the initial systems check can be performed. See section 4.3.1 through 4.3.10.

4.2.1.1 Set coulometer switches as follows:

Mode: 15 (Calibration)
Time: 10.0 Minutes
Run/Latch: Latch
Counts/Time: Counts

4.2.1.2 Place shorting strap between Red & Black Terminal outlets, connecting Red-to-Red & Black-to-Black.

4.2.1.3 Turn on main power switch & cell current.

4.2.1.4 Rotate %T adjustment until approximately 200 ± 5 mA of current is seen on the digital current meter. Consult systems manual and/or cognizant scientist if problems arise.

4.2.1.5 Depress the reset lever.

Every 10 seconds the digital volt meter (DVM) should freeze at approximately 100,000 ± 500. If the value displayed is out of range, recheck the settings on the coulometer, and repeat the test. If further difficulties are encountered, consult cognizant scientist and/or systems manual.

4.3 Cell Filling and Cell Startup

4.3.1 Fill the body of the coulometer cell with 50-100 ml of coulometer cathode solution.

4.3.2 Place the stir bar (magnet) in the bottom of the cell body.

4.3.3 Insert the cell top, which contains the coiled platinum electrode into the cell.

4.3.4 Add approximately 1/4" layer of potassium iodide (KI) to the bottom of the side arm (anode compartment) of the coulometer cell.

4.3.5 Fill the anode compartment with approximately 12-20 ml of coulometer anode solution.

4.3.6 Place the solid silver electrode in the anode compartment with the silver in the solution.

4.3.7 Place the assembled cell in the coulometer cell holder. The cell shall be positioned with the anode compartment extending out of the front of the holder and the platinum electrode and cell pointing toward the back of the holder, out of the light path.

4.3.8 Turn on the main power switch.

4.3.9 Rotate the cell until a maximum % Transmittance (%T) is achieved.

4.3.10 Adjust the %T until the %T meter shows 100%.

4.3.11 Attach the electrodes to the cell outlet terminals connecting red to red and black to black. (Red = Anode and Black = Cathode).

4.3.12 Turn on the coulometer cell current.

4.3.13 Allow the cell current to titrate the cell solution to its end point (solution color becomes blue with a %T of approximately 29). (Coulometer cathode solution shall be replaced daily or when over 100 mg of C has been titrated.)

4.4 Oxygen Prescrubber Filling (KOH Scrubber)

4.4.1 Remove the dispersion tube, bushing and the O-ring from the KOH scrubber assembly.

4.4.2 Place 15 to 20 ml of the KOH solution in the body of the KOH scrubber. (45% [wt/vol] KOH)

4.4.3 Replace the dispersion tube, O-ring and bushing. Slide the dispersion tube through the bushing and O-ring so the fritted end is near the bottom of the scrubber.

4.4.4 Hand tighten the bushing/O-ring seal and place the filled scrubber in its holder.

The KOH solution shall be changed about every two weeks or when the solution becomes thick and foamy. If a fresh KOH solution is foamy, dilute the solution with deionized water.

4.5 Magnesium Perchlorate Post Scrubber (Filling)

4.5.1 Remove the silicone scrubber tube fittings from the glass scrubber tube.

4.5.2 Place a small plug of quartz wool into one end of the tube.

4.5.3 Fill the tube with gently packed magnesium perchlorate.

4.5.4 Secure the perchlorate into the tube with another small plug of quartz wool.

4.5.5 Replace the silicon rubber tube fittings and attach the tube to the post-combustion scrubber panel.

Magnesium perchlorate will form a solid mass when it becomes hydrated. This mass can cause a block in the system and shall be changed on a daily basis, or when the gas flow through the tube becomes blocked.

4.6 NOx Scrubber Filling

4.6.1 Remove the silicone scrubber tube fittings from the scrubber tube.

4.6.2 Place a small plug of quartz wool in one end of the tube.

4.6.3 Fill 2/3 of the tube with acid dichromate, and secure it in place with another quartz wool plug.

4.6.4 Fill the remaining 1/3 of the scrubber tube with MnO_2 and secure it in place with another quartz wool plug.

4.6.5 Replace the silicone scrubber tube fittings and attach the tube on the post-combustion scrubber panel.

The NO_x scrubber shall be changed if it becomes wet or when a green cast is apparent in about 75% of the acid dichromate (indicating the dichromate is spent). There is no visible indication that the MnO_2 is exhausted and shall be changed when the dichromate is replaced.

4.7 Set Oxygen Flow

Regulate the pressure of the oxygen supply to 5-10 psi, and set the oxygen flow at 75-125 cc/min on the flow meter. Make sure all oxygen lines are connected and leak free.

4.8 Furnace Settings

4.8.1 Move the three-position switch on the furnace (figure VII in Instrumentation Manual System 150) to the upper position to turn on both the fan and the heat.

4.8.2 Set the furnace temperature to the desired value by depressing the button on the temperature controller and turning it at the same time until the desired temperature value appears on the display.

4.8.2.1 For total carbon analysis set the furnace temperature to between 900 and 1000°C. Nominal is 1000°C.

4.8.2.2 For total organic carbon analysis set the furnace temperature to between 500 and 750°C. Nominal is 600°C.

4.9 Mode Selection Thumbwheel Setting

For the mode selection setting refer to section: Model 5011, Page 3 of the . . . Instruction Manual System 150 . . . for settings (usual setting is position 2).

4.10 Run Latch Mode Setting

Set the run latch mode switch to latch. This will freeze the display at the end of each run.

4.11 Time Set Switch

4.11.1 Set the time switch to 10.0 minutes. (Length of time needed to run samples varies from sample to sample. Familiarity and experience with the equipment will give the operator knowledge of the best times to use. It may be prudent to pre-run samples to determine analysis time required and best approximate sample size.)

4.11.2 Record length of time used to run the samples in the TOC LRB.

4.12 Sample Analysis - Solid (Organic and Total Carbon)

4.12.1 Set up the instrument according to steps 4.3 through 4.9 (step 4.8 will give the furnace setting for either organic or total carbon).

4.12.2 Blank determination: Insert the ladle with the empty platinum boat (see note on alternate boat in section 4.12.9) into the furnace tube and replace the endcap (hand tight only). Do not push the ladle into the furnace heat zone.

4.12.3 Wait until background noise drops to normal levels (approximately 1-2 minutes), then slide the ladle into the heat zone. (This allows CO_2 introduced upon opening of the system, to be removed.)

4.12.4 Push the coulometer reset.

4.12.5 When all the CO_2 has been evolved and titrated, (recognized by a 1. stable coulometer reading or 2. a reading equal to the blank count rate, or 3. at the end of the pre-set time), remove the ladle from the furnace and allow the ladle to cool before beginning the next analysis. Record the value on the digital volt meter (DVM) in the LRB.

4.12.6 Repeat the blank determination until consecutive determinations differ by less than 0.5 μg for every 10 minutes of analysis time (i.e.- A 20 minute analysis would require consecutive blank values differ by less than 1.0 μg C). Record the blank data in the TOC LRB.

4.12.7 Standard Analysis: Weigh a standard into a platinum boat.(See note on alternate boat in section 4.12.9) Place the boat into a cool ladle. Record weight of standard and identification of balance in LRB.

Standard should contain approximately 1.5 to 3 mg of carbon.
Currently no EPA standards for TOC are available. Kodak *a*- D-Glucose is being used as a standard. ~~(Typical recovery rates have been approximately 92 to 97%.) If less than 90%, stop and contact cognizant scientist.~~ Standard recoveries should be 89-104%. If these recoveries cannot be met, consult the systems manual and/or cognizant scientist.

4.12.8 Repeat steps 4.12.2 through 4.12.5, using standards. The number of standards to be run will be determined by the analyst or customer specifications. Normally, a minimum of two standards every 8 hour shift shall be run.

4.12.9 Weigh the sample into a platinum boat. Alternatively, a ceramic boat may be used if sample attacks or reacts with platinum. Optimal sample weight will depend upon quantity of carbon in sample. For unknown material, nominal sample weight is 100 mg. This amount may require being increased or decreased, as directed by cognizant scientist. Record weight of sample and tared boat and indentification in LRB. Place the boat into a cool

ladle. Record weight of sample and balance identification (if different from step 4.12.7) in LRB.

4.12.10 Repeat steps 4.12.2 through 4.12.5, using samples.

4.12.11 Calculations:

$$\% \text{ Carbon} = \frac{(\text{display value in } \mu g \text{ C}) - (\text{blank value in } \mu g \text{ C})}{\text{sample weight in } \mu g} \times 100 \left(\frac{1}{\text{Recovery Fraction}}\right)$$

The % C should be corrected for the less than 100% recovery of Std. Typically 92-97%.

5.0 References

5.1 Instruction Manual System 150, Coulometrics, Inc. Golden Co 80403.

5.2 E. W. D. Huffman, Performance of a New Automatic Carbon Dioxide Coulometer, Microchemical Journal, 22, 567-573 (1977).

5.3 Total and Organic Carbon by Coulometric Detection, ASTM D-4129-82.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-381, DETERMINATION OF TC, TOC, AND TIC IN RADIOACTIVE LIQUIDS, SOILS, AND SLUDGES BY HOT PERSULFATE METHOD (Replaces 7-40.47)

APPLICABILITY

This test procedure covers the determination of total carbon (TC), total organic carbon (TOC) and/or total inorganic carbon (TIC) in a variety of sample types, including liquids, soils, sludges and solids, as would particularly be expected from radioactive waste storage tanks. The radiation involved may range from mildly radioactive liquids, which may be handled in a fume hood, to intense, gamma-active sludges, requiring shielded cell operation. This test procedure covers the oxidation/extraction method of hot persulfate oxidation. This oxidation/extraction method will cause oxidation of carbon species present, including organic species as well as inorganic carbonates, excluding elemental carbon, such as graphite. The percent recovery must be determined by standard analysis. The method allows a two step process providing TOC and TIC on the sample. High caustic levels or high fluoride causes no interference or instrumental problems.

Original references for the hot persulfate procedure are included in Section 2.0, references 2.3 - 2.6.

DEFINITIONS

LRB - Laboratory Record Book

RESPONSIBLE STAFF

Cognizant Scientist

Responsible for providing information to Analyst or changing experimental conditions, as noted in procedure, dependent upon sample requirements.

Analyst

Responsible for performing step-by-step procedure.

Author DL Baldwin Date 2/24/92	Project Mgr. BM Gillespie Date 2/25/92	QAD Representative BO Barnes Date 2/24/92
Technical Reviewer WC Weimer Date 2/24/92	Line Mgr. AG King Date 2/25/92	Other Date

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PNL-ALO-381	0	FEB 25 1992	1 of 8

PROCEDURE

1.0 Discussion

This procedure uses the oxidation/extraction method of hot acidic persulfate oxidation, followed by measurement with the UIC Coulometrics Carbon Analyzer coulometry detector. Excess potassium persulfate oxidant, added to heated sulfuric acid solution with silver catalyst, causes oxidation of all carbon species. All carbon is oxidized to CO_2, and swept away by the oxygen carrier gas. The gas is carried to the Coulometrics Analyzer, measured, the result calculated and displayed directly in ug carbon. The method uses a Coulometrics Acidification unit, modified for this procedure for the hot persulfate oxidation/extraction, with the operation described in procedure PNL-ALO-380 (Analysis of Solid Samples for Carbonate By Use of Coulometrics Model 5011 Coulometer).

The method provides either a) a one step process resulting in TC on a sample or b) a two step process allowing a separate measurement of TOC and TIC on the same sample. In case a), the persulfate/sulfuric acid converts forms of carbon, organic and inorganic, to CO_2 for measurement. In case b), first the sample is acidified with heated sulfuric acid, converting only inorganic carbon to CO_2, providing the TIC result. Then the reaction flask is opened, the persulfate and silver added, and the flask closed and reheated. The organic carbon is then converted providing the TOC result.

Original references for the hot persulfate procedure are included in Section 2.0, references 2.3 - 2.6.

1.1 Apparatus and Reagents

1.1.1 Coulometrics, Model 5030 Acidification Apparatus

1.1.2 Sulfuric acid, 4 N (2 M); prepare by diluting 110 (±5) mL of concentrated, reagent-grade sulfuric acid to 1000 (±5) mL with deionized water.

1.1.3 Potassium persulfate, (potassium peroxydisulfate), crystals, reagent-grade.

1.1.4 Silver nitrate, 2 M; prepare by dissolving 34 (±0.1) g of reagent-grade $AgNO_3$ in 100 (±1) ml of deionized water.

1.1.5 Ascarite for the removal of CO_2 from oxygen carrier gas.

1.2 Preparation

1.2.1 Set up Coulometrics Acidification unit for normal operation per Procedure 7-40.36 (Analysis of Solid Samples for Carbonate By Use of Coulometrics Model 5011 Coulometer). Connect outlet gas line to coulometer.

1.2.2 Set up Coulometrics Coulometer Analyzer for normal operation per procedure 7-40.37.

1.2.3 Prepare all reagents for operation, i.e., solid persulfate, silver nitrate, sulfuric acid in pipettor container, etc.

1.2.4 Turn on the power switch to the coulometrics 5030 unit.

1.2.5 Set the heater to 60%. This can be increased or decreased as specified by the cognizant scientist. Record change in LRB.

1.2.6 Set the INT/EXT switch to INT.

1.3 Initial Systems Check

1.3.1 Set Coulometer switches as follows:

Mode: 15 (calibration)
Time: 10.0 minutes
Run/Latch: Latch
Counts/Time: Counts

1.3.2 Place shorting strap between red & black terminal outlets, connecting red-to-red & black-to-black.

1.3.3 Turn on both main power switch & cell current.

1.3.4 Rotate %T (transmittance) adjustment until approximately 200±5mA of current is seen on the Digital Current Meter. Consult cognizant scientist and/or systems manual if problems arise.

1.3.5 Depress the reset lever.

Every 10 seconds the digital volt meter (DVM) should freeze at approximately 100,000 ± 500. If the value displayed is out of range, recheck the settings on the coulometer and repeat the test. If further difficulties are encountered, consult cognizant scientist and/or systems manual.

1.4 Coulometer Set-Up

1.4.1 Turn on the main power switch

1.4.2 Rotate the cell until a maximum % transmittance (%T) is achieved.

1.4.3 Adjust the %T until the meter shows 100%.

1.4.4 Attach the electrodes to the cell outlet terminals connecting red to red and black to black. (red = anode and black = cathode).

1.4.5 Turn ON the coulometer cell current.

1.4.6 Allow the cell current to titrate the cell solution to its end point (solution color becomes blue with %T of approximately 29), within 20 minutes.

1.4.7 Rotate the MODE selection thumb wheel to select desired units for analysis. There are sixteen (16) possible MODE selections. More information on the derivation and use of the MODE selections can be found on Table I in the section titled, ELECTRICAL DESCRIPTION OF SUBASSEMBLIES, of the Coulometrics Instruction Manual System 150.

The following units are available:

0	Cts	direct coulometer counts.
1	µg C	micrograms carbon (C) to 0.1 units.
2	µg C	micrograms carbon (C) to 0.01 units.
3	mg C/L	milligrams carbon/liter to 0.1 units for a 0.2 ml injection.
4	µg CO_2	micrograms CO_2 to 0.1 units.
5	µg CO_3	micrograms CO_3 to 0.1 units.
6	µg O	micrograms oxygen (O) to 0.1 units.
7	µg H	micrograms hydrogen to 0.1 units.
8	µg H_2O	micrograms water to 0.1 units.
9	µg equiv.	microgram equivalent to 0.1 units.

10	mg C/L um	milligrams carbon/liter to 0.1 units for manual operation of the Model 5090.
11	mg C/L am	milligrams carbon/liter to 0.1 units for automated operation of the Model 5090.
12	µg C c/c	micrograms carbon to 0.1 units for automated operation of the Model 102-C, 105-C and 106-C.
13	OPT A	option
14	OPT B	option
15	Calib	calibration mode

Position 2 is the selection being used for this method.

1.4.8 Rotate the TIME SET thumb wheel to the desired analysis time, twenty (20) minutes, or as specified by cognizant scientist.

1.4.9 Set the RUN/LATCH switch in the LATCH position for timed analyses.

1.4.10 Set the COUNTS/TIME switch to the COUNTS position.

The digital display will show the current measurement in the units selected in step 1.4.7. If the switch is in the TIME position, the display will show the lapsed time since the last reset.

1.4.11 Set the carrier gas (oxygen) flow to 75-100 cc/min.

1.5 Blanks, Standards, Samples

1.5.1 Blanks, standards and samples shall be analyzed identically. Separate TIC and TOC blanks are required.

1.5.2 Consecutive blanks should agree within 10 ug to be considered stable. 2 or 3 blanks are generally sufficient.

1.5.3 TIC and TOC standards used shall be as specified by cognizant scientist and recorded in LRB.

1.5.4 Run at least two standards each for both TIC and TOC. Compare results obtained for consecutive standards. If they agree within 3 % relative, proceed. If not, repeat standards until 3 % agreement is reached.

1.5.5 If recoveries are satisfactory (90-102%), proceed to the analysis of samples. If not, consult cognizant scientist before proceeding.

1.5.6 Run samples, using Section 1.6. If duplicate samples are to be run, then a single analysis of each is sufficient. If singular sample is to be run, then duplicate analyses will be performed on it (unless the customer or cognizant scientist specifies differently).

1.6 Analysis

1.6.1 Load sample flask with material to be analyzed, or leave empty for blank run. Record weight to ±0.0001g or volume to ± 1 ul in LRB. Typical sample weight is 50-150mg.

1.6.2 If total carbon (TC) only is to be analyzed go to step 1.6.8. For TIC analysis continue to next step.

1.6.3 Install flask and allow system to purge of CO_2 (approx. one minute).

1.6.4 Inject 2-10 ml (consult cognizant scientist as to correct amount) of sulfuric acid into flask and IMMEDIATELY reset coulometer. Lower flask into heater well.

1.6.5 When all of the CO_2 has been evolved and titrated (stable coulometer display or end-of-time locked result), record the displayed value. Calculate the amount of inorganic carbon (TIC) in the sample (or standard) according to:

Standard: Recovery factor (TIC) = $\frac{\mu gC \text{ (displayed)} - \mu gC \text{ (blank)}}{\text{ug C in TIC standard}}$

TIC: % Carbon (TIC) = $\frac{\mu gC \text{ (displayed)} - \mu gC \text{ (blank)} \times 100}{\text{wt. sample (ug)} \times \text{Recovery Factor}}$

1.6.6 Record calculations and results in LRB.

1.6.7 Raise sample flask from heater well and open.

1.6.8 Add 2.0 ±0.1 g solid persulfate to flask. Add 100 ± 5µg silver nitrate solution to flask IMMEDIATELY and QUICKLY AS POSSIBLE install and close flask.

1.6.9 IMMEDIATELY reset coulometer.

1.6.10 If analyzing for total carbon (TC) only, allow system to purge for one minute. If analyzing for TOC, allow no purge time. Reset coulometer if analyzing for TC.

1.6.11 For TOC inject 2-5 ml (consult cognizant scientist as to correct volume) of sulfuric acid into flask. If TC inject 2-10 ml (consult cognizant scientist). Lower flask into heater well.

1.6.12 When all of the CO_2 has been evolved and titrated (stable coulometer display or end-of-time locked result), record the displayed TC or TOC value. Calculate the amount of total carbon or organic carbon (TC or TOC) in the sample (or standard) according to:

Standard: Recovery (TC or TOC) = $\frac{\mu gC \text{ (displayed)} - \mu gC \text{ (blank)}}{\text{ug C in standard}}$

TC or TOC: % Carbon (TOC or TC) = $\frac{\mu gC \text{ (displayed)} - \mu gC \text{ (blank)}}{\text{wt. sample (ug)} \times \text{Recovery Factor}} \times 100$

1.7 Procedure Qualification

This procedure is considered self-qualifying due to its dependence on analytical standards and is considered qualified through the independent technical review of the procedure.

2.0 REFERENCES

2.1 Instrument Manual Systems 150, Coulometrics Inc., Golden, CO.

2.2 E.W.D. Huffman, Performance of a New Automatic Carbon Dioxide Coulometer, Micro-chemical Journal, 22, 567-573 (1977).

2.3 P.D. Goulden, D.H.J. Anthony, "Kinetics of Uncatalyzed Peroxydisulfate Oxidation of Organic Material in Fresh Water", Analytical Chemistry, vol. 50, No. 7, June 1978, p. 953.

2.4 J.M. Baldwin, R.E. McAtee, Microchem. J., 19, 179 (1974).

2.5 P.D. Goulden, P. Brooksbank, "Automated Determinations of Dissolved Organic Carbon in Lake Water", Analytical Chemistry, 47, p 1943, (1975).

2.6 W.S. Updegrove, J.M. Baldwin, "Wet Chemical Oxidation Method for Carbon Determination in Ferrous Alloys", Analytical Chemistry, 45, No. 12, Oct 1973, p 2115.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-383, (Replaces 7-40.36 & PNL-SP-78), ANALYSIS OF SOLID SAMPLES FOR CARBONATE BY USE OF COULOMETRICS MODEL 5011 COULOMETER

1.0 APPLICABILITY

This procedure can be used for determining carbonate in solid samples. Inorganic carbon levels from ppm to pure carbonate can be determined by this procedure.

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Analyst
Cognizant Scientist

4.0 PROCEDURE

4.1 Equipment and Materials

- Model 5011 Coulometrics Coulometer
- Model 5030 Coulometrics Carbonate Carbon Apparatus
- 45% (Wt/Vol) KOH solution
- 50% KI Solution (acidified to pH 3)
- 2N H_2SO_4
- KI crystals
- Coulometer anode solution (proprietary)
- Coulometer cathode solution (proprietary)
- Analytical balance (0.1 mg)

4.2 Description of Procedure

Samples are acidified in a heated reaction vessel to evolve inorganic carbon in the form of CO_2. Carbon dioxide - free air sweeps the CO_2 through a scrubbing system into the CO_2 coulometer for detection.

Author	Date	Project Mgr.	Date	QAD Representative	Date
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Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	8/1/89	All original signatures on file	

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4.3 Cell Filling

4.3.1 Fill the body of the coulometer cell with 50-100 ml of coulometer cathode solution.

4.3.2 Place the stir bar (magnet) in the bottom of the cell body.

4.3.3 Insert the cell top, containing the coiled platinum electrode, into the cell. Position the top with the electrode on the side opposite the fritted side arm.

4.3.4 Add approximately a 1/4" layer of potassium iodide to the bottom of the side arm (anode compartment) of the coulometer cell.

4.3.5 Fill the anode compartment with approximately 12-20 ml of coulometer anode solution.

4.3.6 Place the solid silver electrode in the anode compartment with the silver in the solution.

4.3.7 Place the assembled cell in the coulometer cell holder.

The cell should be positioned with the anode compartment extending out the front of the holder and the platinum electrode and cell pointing toward the back of the holder, out of the light path.

4.4 KOH Scrubber (air scrubber) Filling

This scrubber is used to remove CO_2 from the air (carrier gas). A solution of 40-45% (wt/vol) potassium hydroxide (KOH) is a satisfactory scrubbing solution.

The KOH solution should be changed once every week during regular use or when the solution becomes thick and foamy. If a fresh KOH solution is foamy, it should be diluted with deionized or distilled water.

4.4.1 Weigh out 40-45 grams of KOH and dissolve in 100 ml with deionized or distilled water.

4.4.2 Remove the dispersion tube, bushing and O-ring from the KOH scrubber assembly.

4.4.3 Place 15-20 ml of KOH solution in the body of the KOH scrubber.

4.4.4 Replace the dispersion tube, O-ring and bushing. Slide the dispersion tube through the bushing and O-ring so the fritted end is near the bottom of the scrubber.

4.4.5 Hand tighten the bushing/O-ring seal and place the filled scrubber in its clamp.

4.5 Sample Scrubber Filling

Common product gases from the acidification of most materials can be removed with one of the following scrubber solutions:

a. Saturated silver sulfate (Ag_2SO_4) acidified to pH 3.

b. Three percent silver nitrate ($AgNO_3$) acidified to pH 3.

c. Fifty percent Potassium Iodide (KI) acidified to pH 3.

KI is the scrubbing solution that is currently used.

The scrubber solution should be changed on a weekly basis during regular use, or if the frit becomes clogged, or if the analysis blanks become very high.

4.5.1 Weigh out the appropriate amount of chemical to prepare 100 ml of scrubbing solution.

a. Ag_2SO_4 - 3-6 grams

b. $AgNO_3$ - 3 grams

c. KI - 50 grams

4.5.2 Dissolve the chemical in approximately 100 ml of deionized or distilled water.

4.5.3 Fill the fritted sample (silver) scrubber with 10-15 ml of the scrubbing solution.

4.5.4 Acidify the solution in the scrubber to approximately pH 3.

Sulfuric acid is recommended for the acidification of scrubber solutions.

4.5.5 If using one of the silver solutions, add 1 ml of 30% hydrogen peroxide (H_2O_2) to the solution in the scrubber on a daily basis.

4.6 Acid for CO_2 Evolution - Preparation and Filling

A variety of mineral acids can be used for the evolution of CO_2. Depending on the sample composition, certain acids may have advantages over others. The following acids can be used. The proper acid should be selected by the cognizant scientist.

- Sulfuric Acid (2N H_2SO_4) - Precipitation of sulfates may occlude some of the sample's inorganic carbon.
- Perchloric Acid (2N $HClO_4$) - Non-oxidizing in a dilute solution. Most perchlorate salts are soluble. Care should be taken to avoid concentrating the acid.
- Hydrochloric Acid (2N HCl) - HCl from the acid can overload the scrubber. If HCl is used an auxiliary scrubber is recommended.

(The method is currently being run using 2N H_2SO_4.)

With some samples it is often desirable to add a dispersing agent to aid in the wetting or solubilizing of the sample. Aerosol OT proprietary is often used.

Antifoam agents such as Dow-Corning Emulsion AF can be used if sample foaming is troublesome.

When there is concern about the oxidation of organic materials in a sample (as in soil analysis), antioxidants, such as $SnCl_2$ or $FeSO_4$, can be added.

For special applications, other acids and/or differing acid concentrations may be desirable. Contact the cognizant Scientist for correct application of the various acids. Record the acid used in the appropriate LRB.

4.7 Instrument Set up

4.7.1 Turn on the main power switch

4.7.2 Rotate the cell until a maximum % Transmittance (%T) is achieved.

4.7.3 Adjust the %T until the %T meter shows 100%.

4.7.4 Attach the electrodes to the cell outlet terminals connecting red to red and black to black. (Red = Anode and Black = Cathode).

4.7.5 Turn ON the coulometer cell current.

4.7.6 Allow the cell current to titrate the cell solution to its end point (solution color becomes blue with %T of approximately 29).

4.7.7 Rotate the MODE selection thumb wheel until the desired units for analysis are displayed. There are sixteen (16) possible MODE selections. More information on the derivation and use of the MODE selections can be found on Table I in the section on ELECTRICAL DESCRIPTION OF SUBASSEMBLIES, of the Coulometrics instruction manual system 150.

The following units are available:

0	Cts	
1	µg C	micrograms Carbon (C) to 0.1 units.
2	µg C	micrograms carbon (C) to 0.01 units.
3	mg C/L	milligrams carbon/liter to 0.1 units for a 0.200 ml injection
4	µg CO_2	micrograms CO_2 to 0.1 units.
5	µg CO_3	micrograms CO_3 to 0.1 units
6	µg O	micrograms oxygen (O) to 0.1 units.
7	µg H	micrograms hydrogen to 0.1 units.
8	µg H_2O	micrograms water to 0.1 units.
9	µg equiv.	microgram equivalent to 0.1 units.
10	mg C/L um	milligrams carbon/liter to 0.1 units for manual operation of the Model 5090.*
11	mg C/L am	milligrams carbon/liter to 0.1 units for automated operation of the Model 5090.*
12	µg C c/c	micrograms carbon to 0.1 units for automated operation of the Model02-C, 105-C and 106-C.
13	OPT A	option
14	OPT B	option
15	Calib	calibration mode

Position 2 is the selection being used for this method.

4.7.8 Rotate the TIME SET thumb wheel until the desired analysis time is displayed. Five (5) minutes is an appropriate length of time.

4.7.9 Set the RUN/LATCH switch in the LATCH position for timed analyses.

4.7.10 Set the COUNTS/TIME switch to the COUNTS position.

The digital display will show the current measurement in the units selected in step #1. If the switch is in the TIME position, the display will show the lapsed time since the last reset.

4.7.11 Turn on the power switch to the coulometrics 5030 unit.

4.7.12 Set the air flow to 75-100 cc/min.

4.7.13 Set the heater to 60%. This can be increased or decreased as recommended by the cognizant scientist.

4.8 Systems Blank

4.8.1 Attach the sample tube and allow the system to purge itself of CO_2 (approximately 1 minute).

4.8.2 Move the sample column into position so the sample tube is in the heater insulating ring.

4.8.3 Dispense 2 ml of acid into the system

4.8.4 IMMEDIATELY reset the coulometer.

4.8.5 When all of the CO_2 has been evolved and titrated (recognized by a stable coulometer display), record the display value.

4.8.6 Repeat steps 4.8.1 through steps 4.8.5 until a stable blank is achieved. Consecutive blanks should agree within 0.5 mg to be considered as stable. Usually 2-3 blanks are sufficient.

4.9 Running Standards and Samples

4.9.1 Charge a known weight of sample or standard into a sample tube. The sample size should be selected so

the sample contains 1-3 mg of inorganic carbon. Standards to be used will be recommended by the cognizant scientist. The analyst will record the manufacturer, the date of expiration and the lot number of the standard in the LRB.

4.9.1.1 Weigh the sample or standard directly into the sample tube. Record weight and balance identification in LRB.

4.9.1.2 The sample tube does not need to be dry, but must be acid-free to prevent premature release of CO_2.

4.9.2 Attach the sample tube and allow the system to purge itself of CO_2 (approximately 1 minute).

4.9.3 Move the sample column into position so the sample tube is in the heater insulating ring.

4.9.4 Dispense 2 ml of acid into the system.

4.9.5 IMMEDIATELY reset the coulometer.

4.9.6 When all of the CO_2 has been evolved and titrated (recognized by a stable coulometer display), record the display value. Calculate the amount of inorganic carbon in the sample (or standard) according to:

$$\% \text{ Inorganic Carbon} = \frac{\mu gC(\text{standard or sample}) - \mu gC\ (\text{blank})}{\text{wt. sample (or standard) in } \mu g} \times 100$$

4.9.7 Run at least 2 standards using steps 4.9.1 through 4.9.6

4.9.8 Compare the results obtained for the standards. If they agree with 3% relative, proceed. If not, run another standard and compare the previous value. Continue in this way until consecutive standards agree within 3% relative.

4.9.9 Compute the percent recovery of carbon in standards.

The formula for the calculation of % recovery is:

$$\% \text{ recovery} = \frac{\%\ \text{inorganic C found (formula in 4.9.6)}}{\%\ \text{inorganic C in standard}} \times 100$$

4.9.10 If recoveries are satisfactory (95-105%), proceed to the analysis of samples. If not, consult the Cognizant Scientist before proceeding.

4.9.11 Run the sample, using steps 4.9.1 through 4.9.6. Only one aliquot of each sample will be run unless the customer specifies differently.

4.10 Procedure Qualification

This procedure is considered self-qualifying due to its dependence on analytical standards and is considered qualified through the Independent Technical Review of the procedure.

5.0 REFERENCES

5.1 Instrument Manual Systems 150, Coulometrics Inc., Golden, CO.

5.2 E. W. D. Huffman, Performance of a New Automatic Carbon Dioxide Coulometer, Micro-chemical, Journal, 22, 567-573 (1977).

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-384, SOXHLET EXTRACTION

APPLICABILITY

This procedure describes the method for extracting nonvolatile and semi-volatile organic compounds from soils/sediment samples or other solid matrices and subsequent preparation of the extract. This procedure may be used to support additional procedures in compliance with EPA Contract Laboratory Program (CLP) or other programs/projects as elected. This procedure is taken directly from the SW 846 Method 3540B.

DEFINITIONS

None.

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

PROCEDURE

See Attachment 1 for the details of the procedure.

Exceptions:

Section 3.0 - For interferences to this method see PNL-ALO-344 for semivolatiles and PNL-ALO-347 for PCB/Pesticides.

Section 4.4 - Boiling chips will be approximately 10/40 mesh (silicon carbide or equivalent) and soxhlet extracted or heated to 400°C for 30 minutes.

Section 4.10 and 7.2 - % solids will be determined by an Analytical Chemistry Laboratory group other than the Organic Group, therefore these sections are not applicable.

Section 7.3 - Method 3500 and 3540B will not be followed for the surrogate and matrix spiking solutions. Refer to technical procedures PNL-ALO-120 for semivolatile and PNL-ALO-347 for PCB/Pesticides.

Author MJ Steele	Date 1-21-93	Project Mgr. NA	Date	PQ Representative TL Ehlert	Date 1/21/93
Technical Reviewer RW Stromatt	Date 1-21-93	Line Mgr. AG King	Date 1-21-93	Other EW Hoppe	Date 1-21-93
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Section 7.12 - SW-846, Section 4.3 of this Chapter will not be followed. Refer to technical procedure PNL-ALO-345 for semivolatile analysis and PNL-ALO-346 for PCB/Pesticides analysis.

Section 8.0 - Chapter one and method 3500 will not be followed. Refer to technical procedure PNL-ALO-345 for semivolatile analysis and PNL-ALO-346 for PCB/Pesticides analysis for appropriate quality control. A method blank, spike, and spike duplicate are required every 20 samples or less, processed at the same time. The client may impose more stringent frequency for these QC samples.

Section 9.0 - Technical procedures PNL-ALO-345 and/or PNL-ALO-346 shall be followed for spike recovery limits and actions taken in the event the recovery is outside these established limits.

SPECIFIC QUALIFICATIONS

This procedure is based on standard, well understood methods and is therefore self qualifying.

RECORDS

Records will be maintained and controlled so as to conform to the requirements of the ACL Quality Assurance Plan, MCS-033.

TOLERANCES

Tolerances for all measurements made during an analysis shall be specified in a manner consistent with the requirements in the ACL Quality Assurance Plan, MCS-033.

REFERENCES

Soxhlet Extraction, SW-846, Method 3540B, Test Methods for Evaluation Solid Wastes, Third Edition, United States Environmental Protection Agency, November 1986.

METHOD 3540B

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water insoluble and slightly water soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor - 40 mm ID, with 500 mL round bottom flask.

4.2 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.6 Vials - Glass, 2 mL capacity, with Teflon lined screw or crimp top.

4.7 Glass or paper thimble or glass wool - Contaminant free.

4.8 Heating mantle - Rheostat controlled.

4.9 Disposable glass pasteur pipet and bulb.

4.10 Apparatus for determining percent dry weight.

4.10.1 Oven - Drying.

4.10.2 Desiccator.

4.10.3 Crucibles - Porcelain or disposable aluminum.

4.11 Apparatus for grinding

4.12 Analytical balance - 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents

5.4.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems:

5.4.1.1 Acetone/Hexane (1:1) (v/v), CH_3COCH_3/CH_6H_{14}. Pesticide quality or equivalent.

NOTE: This solvent system has lower disposal cost and lower toxicity.

5.4.1.2 Methylene chloride/Acetone (1:1 v/v), CH_2Cl_2/CH_3COCH_3. Pesticide quality or equivalent.

5.4.2 Other samples shall be extracted using the following:

5.4.2.1 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.4.2.2 Toluene/Methanol (10:1) (v/v), $C_6H_5CH_3/CH_3OH$. Pesticide quality or equivalent.

5.5 Exchange solvents

5.5.1 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.5.2 2-Propanol, $(CH_3)_2CHOH$. Pesticide quality or equivalent.

5.5.3 Cyclohexane, C_6H_{12}. Pesticide quality or equivalent.

5.5.4 Acetonitrile, CH_3CN. Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analysis, Section 4.1.

7.0 PROCEDURE

7.1 Sample Handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples - Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.1.4 Gummy, fibrous or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling these difficult matrixes.

7.2 Determination of sample % dry weight - In certain cases, sample results are desired based on dry weight basis. When such data is desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (see Method 3500 for details on the surrogate standard and matrix spiking solutions). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel Permeation Chromatography Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.4 Place approximately 300 mL of the extraction solvent (Section 5.4) into a 500 mL round bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles/hr.

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

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

7.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100 to 125 mL of extraction solvent to complete the quantitative transfer.

7.8 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet 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 (15-20°C above the boiling point of the solvent) 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 10-20 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 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add approximately 50 mL of the exchange solvent and a new boiling chip, and reattach the Snyder column. Concentrate the extract as described in Section 7.8, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1-2 mL, remove the K-D apparatus from the water batch and allow it to drain and cool for at least 10 minutes.

7.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the techniques described in Section 7.11 or adjusted to 10.0 mL with the solvent last used.

7.11 If further concentration is indicated in Table 1, either micro Snyder column technique (Section 7.11.1) or nitrogen blowdown technique (Section 7.11.2) is used to adjust the extract to the final volume required.

7.11.1 Micro Snyder Column Technique

7.11.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 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 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of solvent and add to the concentrator tube. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.11.2 Nitrogen Blowdown Technique

7.11.2.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.11.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.12 The extracts obtained may now be analyzed for the target analytes using the appropriate organic technique(s) (see Section 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined screw cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

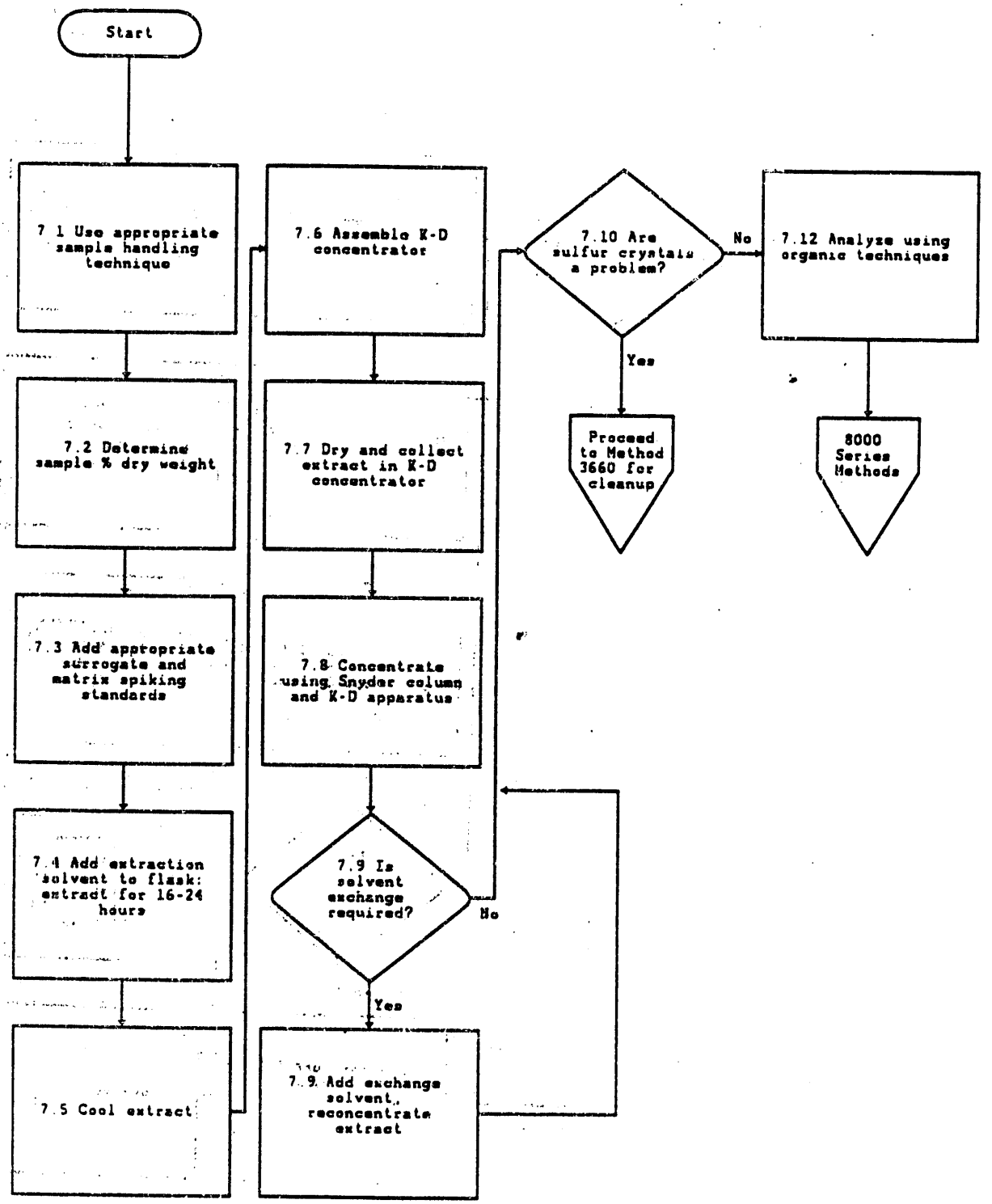
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8110	as received	hexane	hexane	2.0	10.0
8120	as received	hexane	hexane	2.0	1.0
8121	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8141	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	--	--	1.0
8270[c]	as received	none	--	--	1.0
8310	as received	acetonitrile	--	--	1.0
8321	as received	methanol	--	--	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

[a] To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b] Phenols may be analyzed by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optical derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

METHOD 3540B
SOXHLET EXTRACTION



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