ENVIRONMENTAL ASSESSMENT
AT THE
POLLUTION ABATEMENT SERVICES (PAS) SITE
IN
OSWEGO, NEW YORK
APPENDIX A
CLP PROTOCOL

Prepared for :

NEW YORK STATE
DEPARTMENT OF ENVIRONMENTAL CONSERVATION

50 Wolf Road, Albany, New York 12233

Henry G. Williams, Commissioner

DIVISION OF SOLID AND HAZARDOUS WASTE

Norman H. Nosenchuck, P.E. - Director

URS Company, Inc.
570 Delaware Avenue
Buffalo, New York 14202

(c) The Contractor agrees to obtain the written consent of the Contracting Officer, after a written determination by the appropriate program office, prior to entering into any subcontract that will require the subcontractor to collect information. The Contractor agrees to include this clause, including this paragraph (c), and the clause entitled "Treatment of Confidential Business Information" in all subcontracts awarded pursuant to this contract that require the subcontractor to collect information

STATEMENT OF WORK

INORGANICS ANALYSIS
Multi-Media
Multi-Concentration

5/18/82

Statement of Work

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SCOPE OF WORK

The putpose of this conttect is to ptovide EPA with chemical snalytical services nsing inductively coupled plasma (1CP) emission spectroscopy, flameless snd eold vapot stomic shsorption specrroscopy, snd several specified inorgsnic techniques fot the snalysis of field samples, the majority of which will be hszardous waste disposal site samples. These samples are expected to conrsin hszerdous substsnces in concentrstions rsnging from parts per million to 15% nf the total sample. When sn analyte concentration excseds the calibrsted rsnge, resnalysis of the prepared sample after sppropriste dilution is required.

Procedures spscified hersin shall be used in the prepsrstinn snd snalysis of squeous, nonsqueous, solid snd multiphsse samples for the presence snd quantitstion of up to 24 indicsted slements snd inorgsnic species. The Contractor shall employ safe handling procedures snd generally sccspted good laboratory practices in the performance of contract requirements snd shall follow the qualiry sssursnce/quslity control progrsm spscified herein.

The dsts obtsinsd under this contract will be usad by EPA to derermine rhe exisrence snd extent nf threats to the public end the snvironment posed by hszardous wsste disposal sites. The dsts may be used in civil snd/or crimiual litigstion which requires the strictest sdhereuce to chsin-of-cusrody protocol, document control, snd qusliry ssssursnce procsdurss.

EXHIBIT A

SUMMARY OF REQUIREMENTS

General Requirements

The Contractor shall use proved instruments and approved techniques to prepare samples for analysis and to identify and measure the elements and inorganic species presented in Exhibit C.

The Contractor shall perform all analyses including necessary sample preparation procedures as prescribed in Exhibit D, while adhering to requirements for sample containers, preservation protedures and maximum holding times in Exhibit F.

The Contractor shall follow the designated quality assurance and quality control protocol (Exhibit E) and shall employ chain-of-custody and document control procedures in all aspects of sample handling and documentation as specified in Exhibit G.

Following sample analysis, the Contractor shall perform data reduction and shall report analytical activities, sample data, and quality control documentation as designated in Exhibit B.

This analytical activity using procedures specified in this SOW will identify and quantitate the parameters specified in Exhibit C in single and multiphase hazardous waste samples.

Specific Requirements

The Contractor shall provide the required analytical expertise and instrumentation for analyses of the elements and inorganic species equal to or higher than the detection limits specified in Exhibit C. In Exhibit D, EPA provides the Contractor with the specific sample preperation techniques and analytical procedures to be used along with a procedural rationale and a schematic flow chart depicting the complete low level-medium level inorganics analytical scheme.

The Contactor shall analyze samples within the maximum holding time specified in Exhibit F even if these times are less than the maximum 30-day completion time allowed in this contract.

Note: The Contractor is advised that the samples received under this contract may contain higher (greater than 10%) levels of organic and inorganic materials of unknown structure and concentration and should be handled throughout the analysis with appropriate caution.

Methods for preparation of aqueous, non-aqueous, solid and multiphase samples are prescribed in Exhibit D. Pursuant sample analysis is indicated in three separate Tables (Exhibit C) to identify and quantify up to 24 elements and inorganic species.

For each sample received, the Contractor may be required to perform the analyses described in paragraphs 1., 2. and 3., following. (The documentation that accompanies the sample(s) to the Contractor facility shall indicate specific analytical requirements for that sample or set of samples, by task and by specific target parameters.)

For the purpose of this contract, the analysis of a sample is defined as any, or all, of the tasks and constituents identified in Exhibits C and D, and related QA/QC as specified in Exhibit E.

NOTE: All QA/QC requirements are an inherent part of this contract requirement and are included in the contract bid price.

1. In Exhibit D, the Environmental Protection Agency (EPA) provides the Contractor with specific analytical procedures to be used. These include instructions and references for sample preparation of single phase and multiphase samples containing low-to-medium concentrations of inorganics for ICP analysis or alternate method specified (Task 1), flameless and cold vapor AA analysis or alternate methods specified (Task 2), and other inorganic analyses (Task 3). The identification and quantification of elements shall be accomplished using ICP spectroscopy or alternate method for those elements indicated in Exhibit C under Table 1, and by using flameless and cold vapor AA spectroscopy or alternate methods for those elements indicated in Exhibit C under Table 2. The inorganic compound parameters (Table 3) shall be analyzed by the individual procedures specified in Exhibit D.

2. The Contractor shall establish and use on a continuing basis QA/QC procedures including the daily or (as required) more frequent use of standard reference solutions from EPA, the National Bureau of Standards or secondary standards traceable thereto, where available or appropriate concentrations, i.e., standard solutions designed to insure that operating parameters of equipment and procedures, from sample collection through identification and quantification, produce reliable data. Exhibit E specifies the QA/QC procedures required. Additional quality assurance and quality control will be required on a quarterly basis in the form of Intercomparison Study Samples submitted by EPA for analysis. (See Exhibit E.)

3. For the purpose of this contract, one analysis unit by ICP spectroscopy shall be considered the analysis of the appropriate blank samples and standards (with the frequency specified in Exhibit E) and the sample for one or more parameters listed in Exhibit C under Table 1. One analysis unit by flameless and cold vapor AA spectroscopy is the analysis of the appropriate blank samples and standards (with the frequency specified in Exhibit E) and the sample for one or more element listed in Exhibit C

under Table 2. For Table 3, the measure of one or more inorganic compounds and blanks and standards (with the frequency specified in Exhibit E) will be considered as one analysis unit. A full sample analysis shall be considered one or more of the analysis units defined above. Duplicate and spike analyses shall each be considered a separate full sample analysis.

4. The Contractor shall be responsible for any handling or processing required for the receipt of sample shipments, including pickup of samples at the nearest servicing airport, bus station, or other carrier service within the Contractor's geographical area. Sample shipments shall be picked up by the Contractor within twenty-four (24) hours of notification. The Government will pay reasonable costs for the return of sample containers.

5. Definition of a Sample

   A sample consists of all components, perhaps more than one phase, contained inside appropriate receptables. More than one container may be used for a single sample; individual containers may contain preservatives for different analysis portions. Containers may be glass or plastic.

6. The Contractor shall adhere to chain-of-custody and document control procedures described in Exhibit C. Documentation as described therein shall be required to show that all procedures are being strictly followed. This documentation shall be reported for each sample as specified in Exhibit B.

EXHIBIT B

REPORTING REQUIREMENTS AND DELIVERABLES

REPORTING REQUIREMENTS AND DELIVERABLES

The contractor shall provide reports and other deliverables specified hereunder. Specific reports are described below. The matrix which follows the report descriptions gives delivery schedule and report distribution information, including addressees for report designees.

Report Description

A. Weekly Progress Reports - Tabulation of samples received, date of receipt, and a tabulation of problems encountered.

B. Sample Data Package - Data report package for analyses of each sample (including all required QA/QC-Exhibit E) shall include:

1) Tabulated results in ug/L or mg/kg of waste (identification and quantity) of the specified analyses (Exhibit D), validated and signed in original signature by the Laboratory Manager, and reported on Forms I-IV.*

2) Analytical results for waste and extract spikes, duplicates, standards and reagent blanks on QA Forms II, III, IV, V and VI.

3) Tabulation of current calculated instrument detection limits as determined by the laboratory reported on the appropriate QA form.

4) Legible photocopy of raw data (measurement readout record) with sufficient information to unequivocally identify:

a) calibration standards (including prep data)

b) calibration blanks

c) procedure/method blanks

d) samples (by EPA number) and any atypical dilution

e) duplicates

*In the event the Laboratory Manager cannot validate all data reported for each sample, he/she will provide a detailed description of the problems associated with the sample.

f) spikes (indicating standard solutions used, final spike concentrations, volumes involved)

g) any instrument adjustments or apparent anomalies on the measurement record

Information shall include a key to abbreviations, with response units stated, and, where needed, with a cross reference to EPA sample numbers.

C. Results of Intercomparison Study Sample Analyses

Tabulation of analytical results for Intercomparison Study Sample analyses includes all requirements specified in B. above.

D. Document Control and Chain-of-Custody Package

The Document Control and Chain-of-Custody package 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, analysis logbook pages, bench sheets, instrument readout records, computer printouts, raw data summaries, instrument logbook pages, correspondence, and the document inventory.

CONTRACT REPORTING SCHEDULE

	REPORT	# COPIES	DELIVERY SCHEDULE	SMO(1)	EMSL-LV(2)	REGION/ CLIENT(3)
A.	Weekly Progress Report	1	Weekly	X		
B.	Sample Data Package	3	30 days from receipt of samples	X	X	X
C.	Results of Inter-comperison Study Sample Analyses	1	30 days from receipt of samples		X	
D.	Document Control and Chain-of-Custody Package	1	7 days from written request by C.O. or SMO	X		

REPORT DISTRIBUTION ADDRESSEES:

(1) U.S. Environmenral Protection Agency
Contract Laboratory Program
Sample Management Office (SMO)
P.O. Box 818
Alexandria, VA 22313

(2) D.S. Environmental Protection Agency
Environmentel Monitoring Systems Laboratory (EMSL)
P.O. Bnx 15027
Las Vegas, NV 89114

(3) USEPA REGIONS:

REGION I

USEPA Region I
60 Westview Street
Lexington, MA 02173

REGION II

USEPA Region II
S&A Division
Woodbridge Avenue
Edison, New Jersey 08837

REGION III

USEPA Region III
Curtis Building
Sixth and Walnut Streets
Philadelphia, PA 19106

REGION IV

USEPA Region IV
S&A Division
College Station Road
Athens, Georgia 30605

REGION V

USEPA Region V
536 South Clark Street
Tenth Floor, CRL
Chicago, Illinois 60605

REGION VI

USEPA Region VI
First International Building
1201 Elm Street
Dallas, Texas 75270

REGION VII

USEPA Region VII
S&A Division
25 Funston Road
Kansas City, Kansas 66115

REGION VIII

USEPA Region VIII
1860 Lincoln Street
Denver, CO 80295

REGION IX

USEPA Region IX
215 Fremont Street
San Francisco, CA 94105

REGION X

USEPA Region X
1200 Sixth Avenue
Seattle, WA 98101

US ENVIRONMENTAL PROTECTION AGENCY
HWI Sample Management Office
P.O. Box 818 – Alexandria, Virginia 22313
703/557-2490 FTS 8-557-2490

Sample No.

INORGANICS ANALYSIS DATA SHEET

LAB NAME _____ CASE NO. _____

LAB SAMPLE ID. NO. _____ QC REPORT NO. _____

TASK 1 (Elements to be Identified and Measured)

		ug/l or mg/kg (circle one)			ug/l or mg/kg (circle one)
1.	Aluminum		10.	Zinc	
2.	Chromium		11.	Boron	
3.	Barium		12.	Vanadium	
4.	Beryllium		13.	Silver	
5.	Cobalt				
6.	Copper				
7.	Iron				
8.	Nickel				
9.	Manganese				

TASK 2 (Elements to be Identified and Measured)

		ug/l or mg/kg (circle one)			ug/l or mg/kg (circle one)
1.	Arsenic		5.	Mercury	
2.	Antimony		6.	Tin	
3.	Selenium		7.	Cadmium	
4.	Thallium		8.	Lead	

TASK 3 (Elements to be Identified and Measured)

		ug/l or mg/kg (circle one)
1.	Ammonia	
2.	Cyanide	
3.	Sulfide	

COMMENTS:

Inorganics Quality Assurance

QC REPORT KEY:

Case # _____

Sample # _____ _____ _____

CONTRACT REQUIRED DETECTION LIMITS:

Table 1:
(µg/L)

Al	200
Ba	100
Be	5
B	100
Cr	10
Co	50
Cu	50
Fe	50
Mn	15
Ni	40
Ag	10
V	200
Zn	10

Table 2:
(µg/L)

Sb	20
As	10
Cd	1
Pb	5
Hg	0.2
Se	2
Tl	10
Sn	20

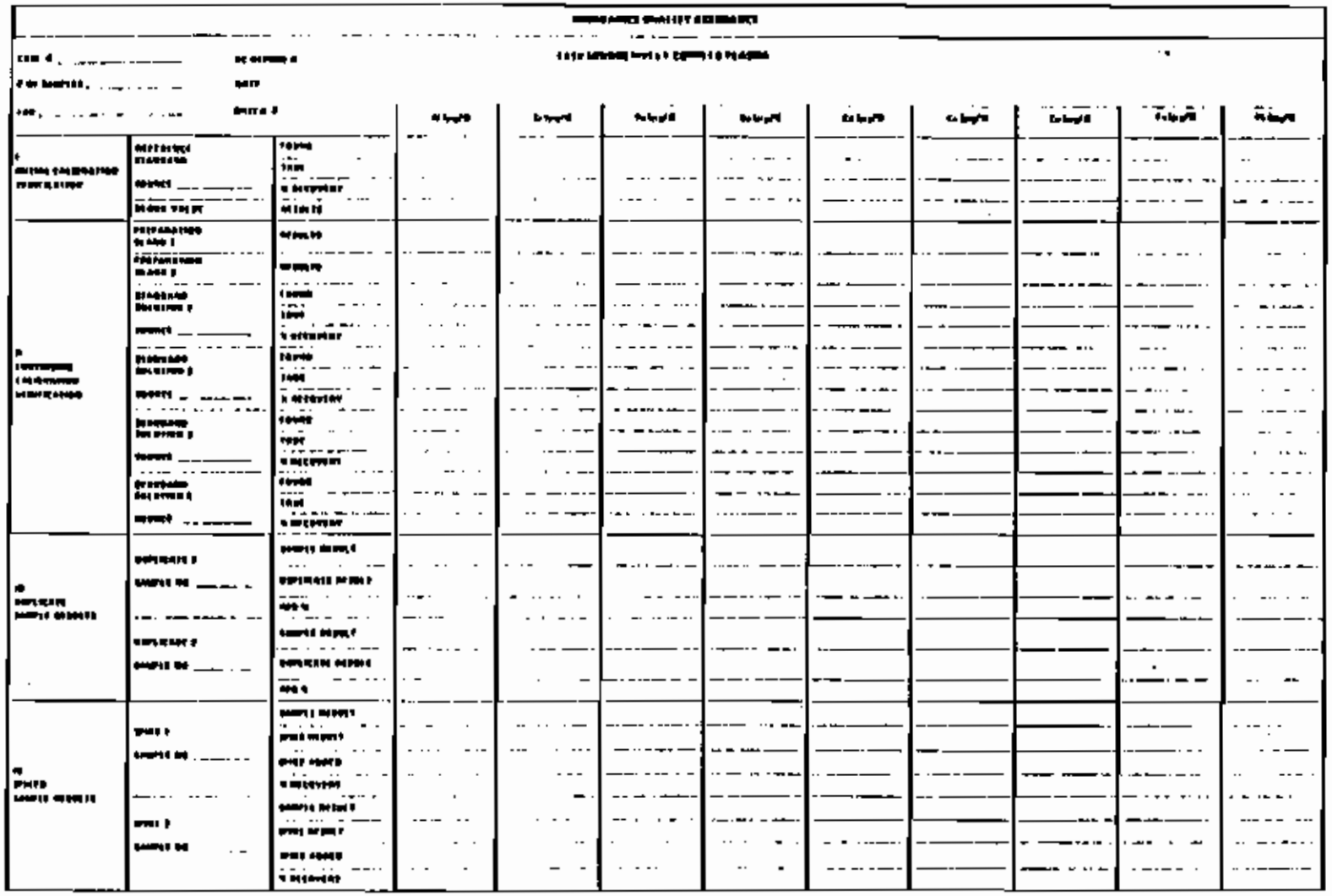
Table 3:
(µg/L)

NH_3	100
CN^{-1}	10
S^{-2}	50

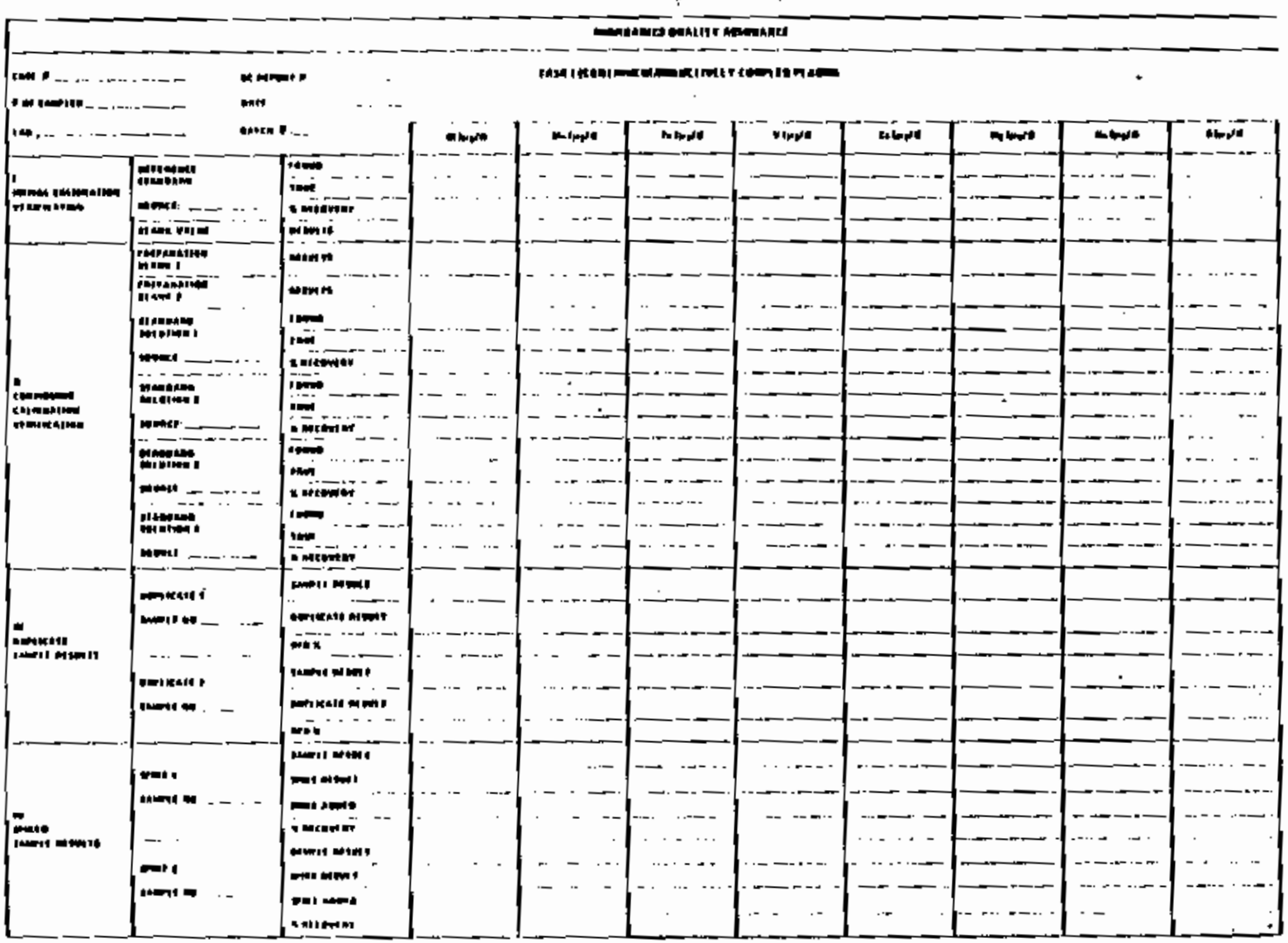
FOOTNOTES:

(1) Spike less than 10 percent of sample concentration.
(2) Loss of analyte during digestion procedure resulted in low recovery; analyte is volatile.
(3) Detection limit raised due to sample matrix interference; actual detection limit is bracketed [].
(4) Sample interference precluded analysis.

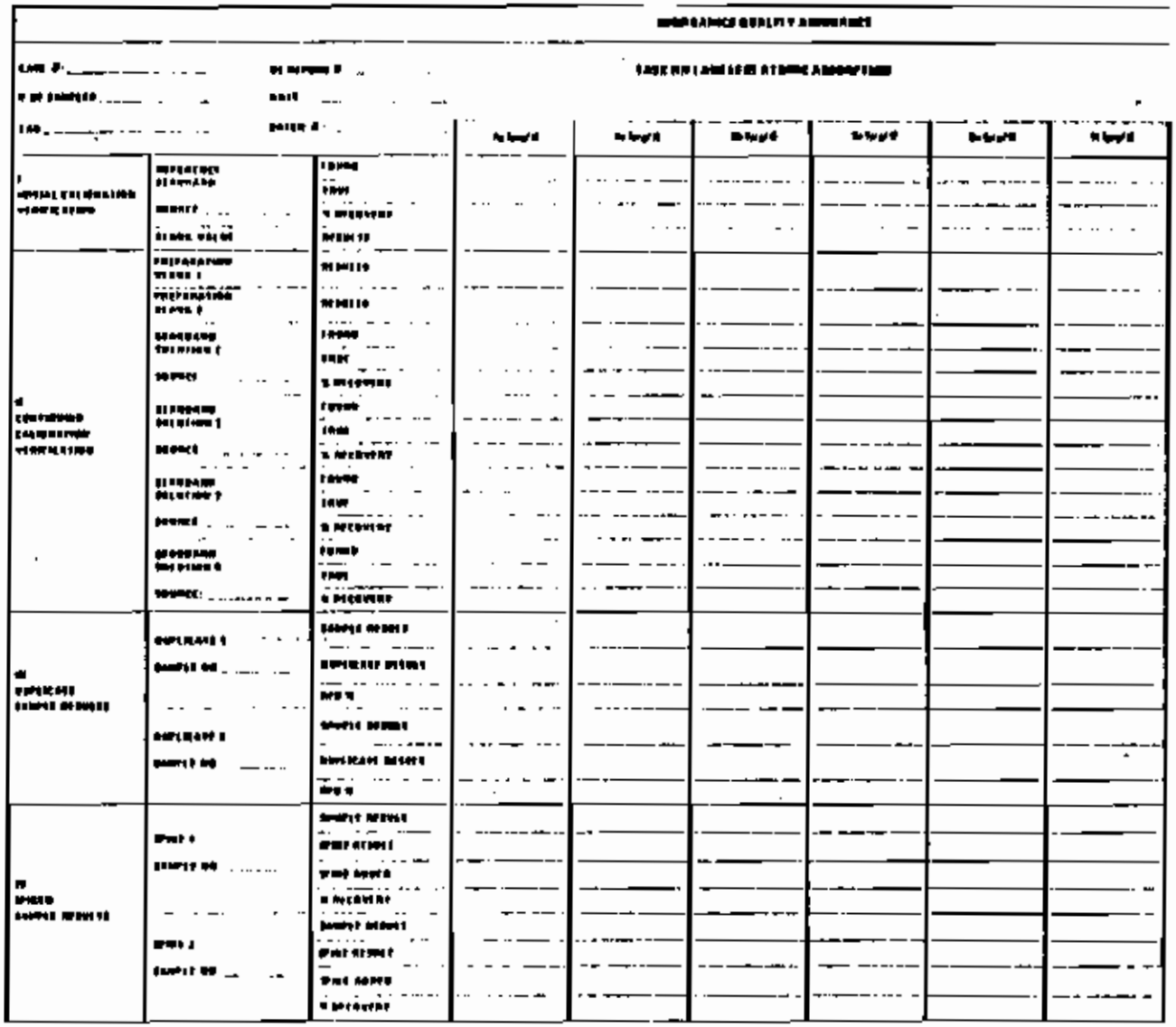
Note: Results reported in brackets [] reflect values calculated which are below required detection limits, but above instrumental detection limits.



Form III



Form III (continued)



Form IV

INORGANICS QUALITY ASSURANCE			
CASE # _____	QC REPORT # _____		TASK II/COLD VAPOR ATOMIC ABSORPTION
# OF SAMPLES: _____	DATE: _____		
LAB: _____	BATCH # _____		[illegible]
I. INITIAL CALIBRATION VERIFICATION	REFERENCE STANDARD SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	BLANK VALUE	RESULTS	
II. CONTINUING CALIBRATION VERIFICATION	PREPARATION BLANK 1	RESULTS	
	PREPARATION BLANK 2	RESULTS	
	STANDARD SOLUTION 1 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	STANDARD SOLUTION 2 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	STANDARD SOLUTION 3 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	STANDARD SOLUTION 4 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
III. DUPLICATE SAMPLE RESULTS	DUPLICATE 1 SAMPLE NO. _____	SAMPLE RESULT	
		DUPLICATE RESULT	
		RPD %	
	DUPLICATE 2 SAMPLE NO. _____	SAMPLE RESULT	
		DUPLICATE RESULT	
		RPD %	
IV. SPIKED SAMPLE RESULTS	SPIKE 1 SAMPLE NO. _____	SAMPLE RESULT	
		SPIKE RESULT	
		SPIKE ADDED	
		% RECOVERY	
	SPIKE 2 SAMPLE NO. _____	SAMPLE RESULT	
		SPIKE RESULT	
		SPIKE ADDED	
		% RECOVERY	

Form V

INORGANICS QUALITY ASSURANCE			
CASE # _____	QC REPORT # : _____		TASK III/AMMONIA
# OF SAMPLES: _____	DATE: _____		
LAB: _____	BATCH # : _____		AMMONIA (mg/l)
I. INITIAL CALIBRATION VERIFICATION	REFERENCE STANDARD SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	BLANK VALUE	RESULTS	
II. CONTINUING CALIBRATION VERIFICATION	PREPARATION BLANK 1	RESULTS	
	PREPARATION BLANK 2	RESULTS	
	STANDARD SOLUTION 1 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	STANDARD SOLUTION 2 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	STANDARD SOLUTION 3 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	STANDARD SOLUTION 4 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
III. DUPLICATE SAMPLE RESULTS	DUPLICATE 1 SAMPLE NO. _____	SAMPLE RESULT	
		DUPLICATE RESULT	
		RPD %	
	DUPLICATE 2 SAMPLE NO. _____	SAMPLE RESULT	
		DUPLICATE RESULT	
		RPD %	
IV. SPIKED SAMPLE RESULTS	SPIKE 1 SAMPLE NO. _____	SAMPLE RESULT	
		SPIKE RESULT	
		SPIKE ADDED	
		% RECOVERY	
	SPIKE 2 SAMPLE NO. _____	SAMPLE RESULT	
		SPIKE RESULT	
		SPIKE ADDED	
		% RECOVERY	

INORGANICS QUALITY ASSURANCE			
CASE #: _____	OR REPORT #: _____		TASK III/CYANIDE
# OF SAMPLES: _____	DATE: _____		
LAB: _____	BATCH #: _____		CYANIDE (mg/l)
I. INITIAL CALIBRATION VERIFICATION	REFERENCE STANDARD SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	BLANK VALUE	RESULTS	
II. CONTINUING CALIBRATION VERIFICATION	PREPARATION BLANK 1	RESULTS	
	PREPARATION BLANK 2	RESULTS	
	STANDARD SOLUTION 1 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	STANDARD SOLUTION 2 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	STANDARD SOLUTION 3 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
	STANDARD SOLUTION 4 SOURCE: _____	FOUND	
		TRUE	
		% RECOVERY	
III. DUPLICATE SAMPLE RESULTS	DUPLICATE 1 SAMPLE NO. _____	SAMPLE RESULT	
		DUPLICATE RESULT	
		RPD %	
	DUPLICATE 2 SAMPLE NO. _____	SAMPLE RESULT	
		DUPLICATE RESULT	
		RPD %	
IV. SPIKED SAMPLE RESULTS	SPIKE 1 SAMPLE NO. _____	SAMPLE RESULT	
		SPIKE RESULT	
		SPIKE ADDED	
		% RECOVERY	
	SPIKE 2 SAMPLE NO. _____	SAMPLE RESULT	
		SPIKE RESULT	
		SPIKE ADDED	
		% RECOVERY	

Form VI (continued)

INORGANICS QUALITY ASSURANCE			
CASE # _____	QC REPORT # : _____		TASK III/SULFIDE
# OF SAMPLES _____	DATE: _____		
LAB: _____	BATCH # _____		SULFIDE (mg/l)
I. INITIAL CALIBRATION VERIFICATION	REFERENCE STANDARD	FOUND	
		TRUE	
	SOURCE: _____	% RECOVERY	
	BLANK VALUE	RESULTS	
II. CONTINUING CALIBRATION VERIFICATION	PREPARATION BLANK 1	RESULTS	
	PREPARATION BLANK 2	RESULTS	
	STANDARD SOLUTION 1	FOUND	
		TRUE	
	SOURCE: _____	% RECOVERY	
	STANDARD SOLUTION 2	FOUND	
		TRUE	
	SOURCE: _____	% RECOVERY	
	STANDARD SOLUTION 3	FOUND	
		TRUE	
	SOURCE: _____	% RECOVERY	
	STANDARD SOLUTION 4	FOUND	
		TRUE	
	SOURCE: _____	% RECOVERY	
III. DUPLICATE SAMPLE RESULTS	DUPLICATE 1	SAMPLE RESULT	
		DUPLICATE RESULT	
	SAMPLE NO. _____	RPD %	
	DUPLICATE 2	SAMPLE RESULT	
		DUPLICATE RESULT	
	SAMPLE NO. _____	RPD %	
IV. SPIKED SAMPLE RESULTS	SPIKE 1	SAMPLE RESULT	
		SPIKE RESULT	
	SAMPLE NO. _____	SPIKE ADDED	
		% RECOVERY	
	SPIKE 2	SAMPLE RESULT	
		SPIKE RESULT	
	SAMPLE NO. _____	SPIKE ADDED	
		% RECOVERY	

Form VI (continued)

EXHIBIT C

CHEMICAL CONSTITUENTS TO BE IDENTIFIED AND MEASURED

TABLE 1. ELEMENTS DETERMINED BY INDUCTIVELY COUPLED PLASMA EMISSION OR ALTERNATE METHOD (Task 1)

Element	Drinking Water Criteria (ug/L)	Required Detection Limit (ug/L)
Aluminum	-	200*
Barium	1000	100
Beryllium	-(P)	5
Boron	-	100
Chromium	50(P)	10
Cobalt	-	50
Copper	1000(a)(P)	50
Iron	300(a)	50
Manganese	50(a)	15*
Nickel	-(P)	40
Silver	50(P)	10
Vanadium	-(H)	200
Zinc	5000(a)(P)	10

(a)Secondary water standard. (P) Priority pollutant. (H) Hazardous Constituent.

*Detection limits of 100 ug/L and 10 ug/L are desired for aluminum and manganese, respectively. The limits achieved must be documented as required in the QC Section, Exhibit E, page 3.

TABLE 2. ELEMENTS DETERMINED BY FURNACE OR COLD VAPOR ATOMIC ABSORPTION, OR ACCEPTABLE ALTERNATES (Task 2)

Element	Drinking Water Criteria (µg/L)	Required Detection Limit (µg/L)
Antimony	-(P)	20
Arsenic	50(P)	10
Cadmium	10(P)	1
Lead	50(P)	5
Mercury	2(P)	0.2
Selenium	10(P)	2
Thallium	-(P)	10
Tin	-	20

(P) Priority Pollutant

TABLE 3. INORGANIC SPECIES TO BE DETERMINED (Task 3)

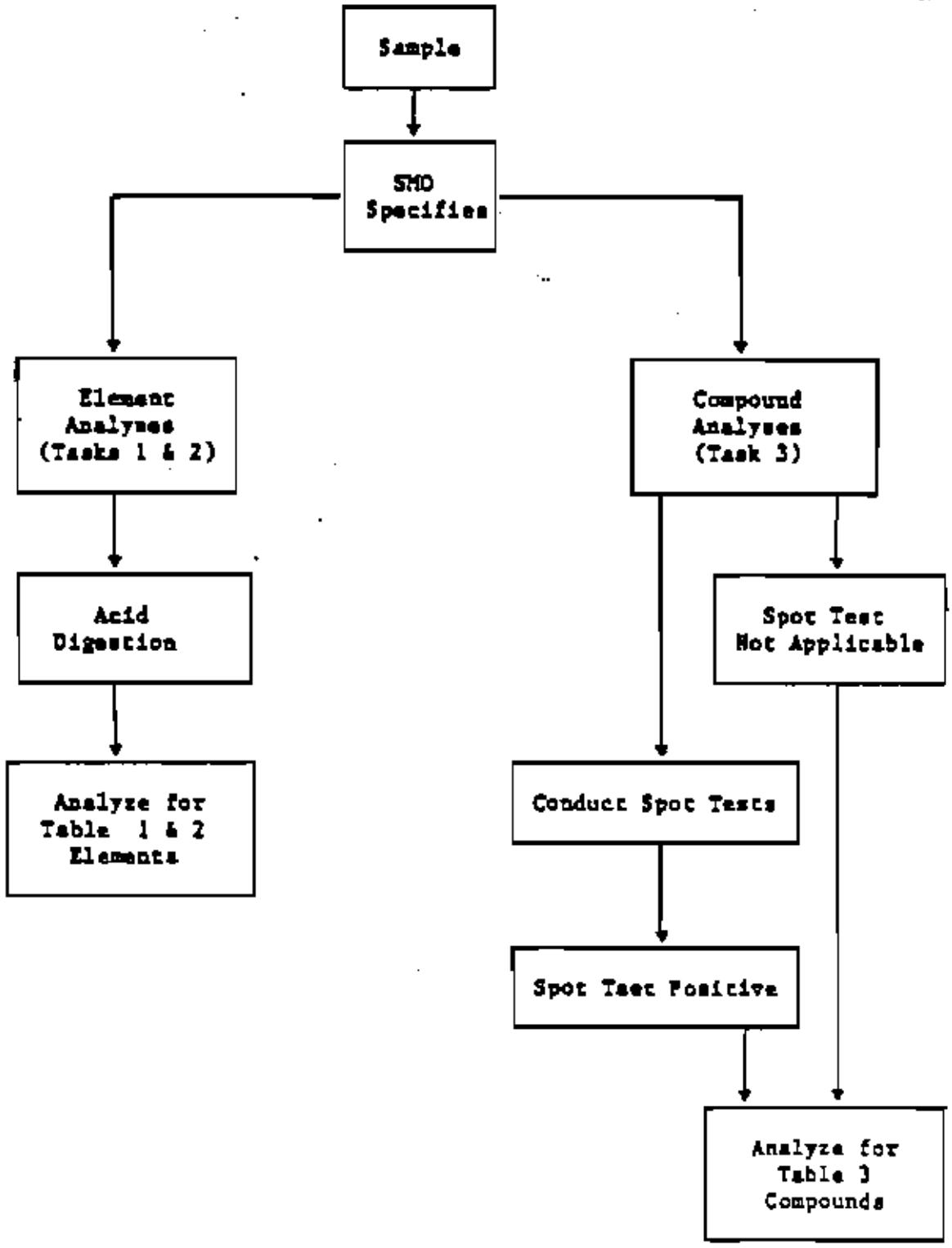
Element	Drinking Water Criteria (µg/L)	Required Detection Limit (µg/L)
Ammonia	-	100
Cyanide	-(P)	10
Sulfide	50	50**

(P) Priority Pollutant
** A detection limit of 10 µg/L is desired, and the limit achieved must be documented as required in the QC Section, Exhibit E, page 3.

EXHIBIT D

ANALYTICAL METHODS

Inorganic Methods Flow Chart



Analytical Methods

NOTE: Reference numbers appear in parentheses throughout this section. See page 4 of this Exhibit for reference list.

1. Element Analyses (Tasks 1 & 2). Acid clean labware according to the EPA water manual (1) or an equivalent procedure.

A. Persulfate digestion is required before the mercury analysis. For aqueous samples use 100 mL for the digestion procedure (2). For other samples (solid, nonaqueous or multiphase) use a 0.2 gram aliquot for the digestion procedure (3). With multiphase wastes a representative aliquot can be obtained by separating and determining the component fractions and by adding together the fractions in the same proportions to produce the aliquot for analysis. When a specific fraction of a multiphase waste should be used in the digestion and analysis, the container label will so indicate.

B. Digestion procedure* described below is required before the analysis of elements other than mercury. However, this procedure is not required for nonaqueous samples (free of metal particles) miscible with methyl isobutyl ketone** (MIBK) or xylene when analysis is conducted by the appropriate methods (4-6) using standards soluble in these organic solvents. When metal particles could be present in the nonaqueous samples (e.g., used engine oil), the digestion in the cited method (6) is required when using the organic-solvent alternative.

For aqueous samples use a 100-mL portion in a 150-mL beaker for the digestion. For other samples (solid, nonaqueous, multiphase) use a 2-gram portion in a 50-mL beaker. Comments on multiphase samples in paragraph A apply here also. If reanalysis is requested using other amounts of the samples (to achieve lower detection limits), apply charge as for a new sample.

In a hood (with the exhaust fan operating) add 10 mL of reagent grade nitric acid (1 + 1) to the sample and evaporate the liquid to near dryness without boiling on a hotplate in the hood. Let sample cool a few minutes, add 8 mL of concentrated nitric acid and again evaporate liquid to near dryness without boiling. Let sample cool a few minutes, add 2 mL of nitric acid (1 + 1) and cautiously add 6 mL of 30% hydrogen peroxide. Warm the sample digest slowly on the hotplate until effervescent reaction subsides. Repeatedly add 1-mL portions of 30% hydrogen peroxide and heat until digestion appears complete (i.e. sample appearance remains unchanged). Let sample cool a few minutes, add 2 mL of nitric acid (1 + 1) and 25 mL of deionized water before warming solution to promote dissolution.

Filter the digest and three 20-mL deionized water rinsings of the beaker through a Whatman #2 (or equivalent) filter paper (washed with two 15-mL portions of 1% nitric acid) into a 100-mL volumetric flask. Add deionized water to the flask until volumetric mark is reached, stopper flask and invert it at least 3 times to mix contents completely. Analyze the peroxide digests

*Derived from an EPA-Cincinnati procedure
**4-methyl-2-pentanone

of the samples for the elements shown in Tables 1 and 2 (Exhibit C) by the methods indicated. The methods for analyzing the digests were selected to provide detection limits that are no more than 20% of the Drinking Water Standard concentrations, where Federal standards exist.

Elements listed in Table 1 (Exhibit C) are determined by flame atomic absorption methods (7,8), a colorimetric method (9) or by the ICP method (10) while elements in Table 2 (Exhibit C) are determined by furnace atomic absorption methods (11) with the exception of mercury (2,3). When the concentration of a Table 2 element in a digest equals or exceeds 5 times the flame atomic absorption or ICP detection limits, measurements by these methods are acceptable alternatives to the furnace atomic absorption method.

2. Compound Analyses (Task 3). Cyanide and sulfide analysis procedures (courtesy of NEIC) are specified for spot tests on both aqueous samples (Attachments 1 and 2, pages 5-8 of this Exhibit) and solid samples (Attachment 3, pages 9-13 of this Exhibit). When spot tests are positive (or upon EPA request), quantitative analyses are conducted for aqueous samples (12 and 13) and solid samples (attachments 4 and 5, pages 14-26 of this Exhibit). When ammonia analysis is requested, follow the specified procedure (14).

When any analyte concentration (for any task) exceeds the calibrated range, reanalyze the prepared sample after appropriate dilution.

References

1. Methods for Chemical Analysis of Water and Wastes (EPA-600/4-79-020), Metals - 4.

2. Ibid, Method 245.1 or 245.2.

3. Ibid, Method 245.5.

4. Fassel, V. A. et al., Anal. Chem. 48(3):516, 1976.

5. Merryfield, R. N. and Loyd, R. C., Anal. Chem. 51(12):1965, 1979.

6. Brown, J. R. et al., Anal. Chem. 52(14):2365, 1980.

7. Op. Cit. (#1), Metals (follows page 180.1-4).

8. Op. Cit. (#1), Method 202.1, 208.1, 210.1, 218.1, 219.1, 220.1, 236.1, 243.1, 249.1, 272.1, 289.1, 286.1, respectively.

9. Op. Cit. (#1), Method 212.3.

10. Federal Register, Vol 44 (233), December 3, 1979, pp. 69559-69564.

11. Op. Cit. (#1), Method 204.2, 206.2, 213.2, 239.2, 270.2, 279.2, 282.2, respectively.

12. Op. Cit. (#1), Method 335.2 or 335.3.

13. Op. Cit. (#1), Method 376.1 or 376.2.

14. Op. Cit. (#1), Method 350.1, 350.2, or 350.3.

Attachment 1

Method 335.61

Spot Test for Cyanide in HWDS Aqueous Phase Samples

1. Scope and Application

1.1 This spot test will detect not less than 0.06 ppm cyanide in aqueous samples. The test needs no more than 3 drops of sample.

1.2 An approximate concentration range can be estimated by comparing samples to sample of known concentration.

1.3 If the sample is highly colored or turbid then Method 335.62/376.62 should be employed.

2. Summary of Method

2.1 Chloramine-T is added to a buffered solution forming cyanogen chloride. Cyanogen chloride forms a red-blue color when mixed with pyridine-barbituric acid.

3. Sample Handling and Preservation

3.1 All sampling should be done in a well-vented hood.

4. Interferences

4.1 Thiocyanate gives the same reaction as cyanide and should be tested separately.

4.2 High reducing chemical content in the sample interferes by consuming the Chloramine-T. Additional Chloramine-T should be added as necessary.

4.3 Aldehydes in excess of 0.5 mg/L interfere by converting cyanide to cyanohydrin.

5. Apparatus

5.1 Plastic disposable 2-mL conical beakers or white spot plate.

5.2 Disposable capillary pipets and rubber bulb.

6. Reagents

6.1 Chloramine-T solution. Dissolve 1 g in 100 mL distilled water. Prepare fresh weekly.

6.2 Pyridine-Barbituric Acid Solution

Place 15 g barbituric acid in a 250 mL volumetric flask, rinse the sides of the flask with a minimum amount of water. Add 75 mL pyridine and mix. Add 15 mL conc. HCl and mix. Add about 140 mL distilled water and stir until all the barbituric acid is dissolved Dilute to mark with distilled water.

6.3 Phosphate Buffer. Dissolve 13.8 g of $NaHPO_4.H_20$ in 100 mL distilled water.

7. Procedure

7.1 For spot test, add 3 drops sample (01-X,Z) to beaker.

7.2 Add one drop phosphate buffer and mix. Check the pH with a pH indicator stick. If the pH is greater than 8 add another drop of buffer and check again. Add buffer until pH is about 8.

7.3 Add one drop Chloramine-T and mix.

7.4 Add one drop pyridine-barbituric acid and mix again.

7.5 A pink to red color will appear after about one minute if 0.06 mg/L or more of cyanide is present. Compare to a blank which will have a faint yellow color.

8. Test Results

8.1 Record the test results on the bench sheet.

8.2 If the test is positive perform Method 335.2 or 335.3 (see reference 12, Exhibit D, page 4) to quantitate the cyanide concentration.

9. Quality Control Requirements

9.1 Daily check the performance of the spot test by analyzing the cyanide spiking solution. If a positive test is not obtained, measures are to be taken to find the problem.

9.2 Perform sample spot test only after a positive test is obtained for 9.1.

9.3 Record the positive standard check on the bench sheet.

Attachment 2

Method 376.61

Spot Test for Sulfide in HWDS Aqueous Phase Samples

1. Scope and Application

1.1 This spot test will detect not less than 4 ppm sulfide in aqueous hazardous waste samples. The test needs no more than one drop.

1.2 If the sample is highly colored or turbid then Method 335.62/376.62 should be employed.

2. Summary of Method

2.1 One drop of the sample is placed on a lead acetate test paper previously moistened with an acetic acid solution. Not less than 4 ppm can be detected.

3. Sample Handling and Preservation

3.1 This procedure should be carried out in the hood.

4. Interferences

None

5. Apparatus

5.1 Disposable capillary pipets and bulbs.

3.2 Small white weighing dish.

6. Reagents

6.1 Lead Acetate Test paper (Fisher Scientific Cat. No. 14-862).

6.2 Acetate Buffer - Dissolve 410 g of sodium acetate trihydrate ($NaC_2H_3O_2$, $3H_2O$) in 500 mL of water. Add glacial acetic acid to pH 4.5.

7. Procedure

7.1 Place a strip of the lead-acetate test paper in a white weighing dish.

7.2 Wet the paper with 2 or 3 drops of the acetate buffer.

7.3 Add one drop sample. A darkening of the test paper indicates the presence of sulfide. Not less than 4 ppm sulfide can be detected.

8. Test Results

8.1 Record the results on the bench sheets.

8.2 If the test is positive then perform Method 376.1 or 376.2 (see reference 13, Exhibit D, page 4) to quantitate the sulfide concentration.

9. Quality Control Requirements

9.1 Daily check the performanne of this spot test by performing the test on a 100 ppm $S^{=}$ standard.

9.2 A positive test must he obtained in 9.1 before analyzing samples.

9.3 Record the positive standard check on the bench sheet.

Attachment 3

Methods 376.62 and 335.62

Spot Test for Sulfide and Cyanide in HWDS Solid Phase Samples

1. Scope

1.1 This procedure allows for a quick screening of semi-solid samples such as a soil or sediment for the presence of 10 ug/g or greater of cyanide and/or sulfide.

1.2 The method, with practice, may be used to indicate relative levels of cyanide and/or sulfide.

1.3 The method detects cyanide in many of the common metallic cyanide complexes. Platinum, gold and cobalt cyanide complexes are not detected as cyanide.

1.4 The method detects all common metal sulfides except those of copper.

2. Summary of Method

2.1 Nitrogen is bubbled through a heated semi-solid sample mixed with $MgCl_2$ and HCl. HCN and H_2S are evolved and pass into a collecting media containing NaOH and $Cd(NO_3)_2$.

2.2 The presence of sulfide is indicated by the discoloration of a lead acetate test strip suspended above the sample; larger amounts of sulfide are indicated by the formation of a yellow precipitate in the collection media.

2.3 Cyanide is indicated using a pyridine barbituric acid technique on the centrifugate from the collection media.

3. Interferences

3.1 The test is specific for cyanide and sulfide since acidification and bubbling releases HCN and H_2S in a reasonably pure state.

3.2 Thiocyanate also responds to the test, however, any thiocyanate resulting in the collection media must be first produced from the reaction of cyanide (from the sample) plus sulfide.

4. Apparatus

4.1 Disposable 1 x 7 cm test tubes.

4.2 Rubber, 2 hole stoppers for the tubes in 4.1.

4.3 Tefloo connecting tube, 1 mm I.D.

4.4 Lead acetate test strips.

4.5 Disposable, long stem eye droppers.

4.6 Surgical rubber tubing, 1/4" I.D.

4.7 Compressed nitrogen and regulator.

4.8 Heating block capable of maintaining 75° ± 5°C with hole openings for the tubes in 4.1.

4.9 Reagents (all reagents made from ACS grade chemicals).

4.9.1 Magnesium chloride solution - Weight 265 g of $MgCl_2.6H_2O$ into 500 mL volumerric flask, dissolve and dilute to volume.

4.9.2 Hydrochloric acid - Dilute 50 mL of concentrated HCl with 50 mL of distilled water; add 0.1 g of aluminum metal.

4.9.3 Cadmium nitrate solution - Dissolve and dilute to 500 mL, 154.5 g of $Cd(NO_3)_2.4H_2O$.

4.9.4 Sodium hydroxide solution - Add 500 mL of distilled water to 40 g of NaOH in a beaker, mix and cool. Transfer the NaOH solution to a 1-liter volumetric flask and dilute to volume.

4.9.5 Methyl Violet Indicator - Dissolve 1 gram of Methyl Violet in 100 mL of ethyl alcohol.

4.9.6 Sodium dihydrogenphosphate, 1 M - Dissolve 138 g of $NaH_2PO_4.H_2O$ in 1 liter of distilled water. Refrigerate this solution.

4.9.7 Pyridine-Barbituric Acid Reagent: Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 15 mL of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

4.9.8 Chloramine-T solution: Dissolve 1.0 g of white, water soluble Chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.

4.9.9 Acetate buffer - Dissolve 410 g of sodium acetate trihydrate in 500 mL of water. Add glacial acetic acid to pH 4.5.

5. Procedure

5.1 Digestion

5.1.1 One gram of sample is weighed into a disposable test tube (02-V) then 1 mL of $MgCl_2$ solution is added; a small glass rod is used to disperse the sample. Apparatus is shown in Figure 1.

5.1.2 One drop of methyl violet is added to the sample tube and a lead acetate test strip moistened with acetate buffer is suspended above the sample between the stopper edge and the lip of the tube.

5.1.3 The apparatus is assembled as in Figure 1 with 1 mL of $Cd(NO_3)_2$ solution and 1 mL of NaOH in tube #2.

5.1.4 Nitrogen is bubbled through the tubes at the rate of 2 bubbles per second for 25 minutes. Temperature of the heating block is 75° ± 5°C.

5.1.5 Four drops (200 µL) of 6N aluminum treated HCl is added to the top of the dropper with the apparatus at an angle such that tubing from the nitrogen supply can be attached to the dropper before the acid hits the sample. The solution should turn yellow or violet coloration should be absent. If not, more acid must be added.

5.1.6 One mL of $MgCl_2$ solution should be analyzed as a blank solution.

5.2 Detection

5.2.1 Any darkening of the lead acetate test strip within 2-3 minutes indicates the presence of sulfide. Yellow coloration in tube #2 indicates higher sulfide concentrations.

5.2.2 Cyanide

5.2.2.1 Centrifuge and transfer the centrifugate from tube #2 to another container.

5.2.2.2 Add 100 µL of sodium dihydrogen phosphate buffer and 100 µL of hydrochloric acid to the centrifugate.

5.2.2.3 Place 3 drops of 5.2.2.2 on a spot plate, add 1 drop of Chloramine-T and mix.

5.2.2.4 Add 1 drop of pyridine barbibturic acid to 5.2.2.3, wait 1 minute. A faint pink to violet color indicates the presence of cyanide.

6. Test Results

6.1 Record the test results on the bench sheet.

6.2 If a positive sulfide test was obtained, then perform Method 376.63 to quantitate the sulfide concenrration.

6.3 If a positive cyanide test was obtained, then perform Method 335.63 to quantitate the cyanide concentration.

7. Quality Control Requirements

7.1 Daily check the performance of this spot test by performing the test on standard CN^- and $S^=$ solution 1 mL each (~100 ppm).

7.2 A positive test must be obtained before analyzing samples.

7.3 Record positive standard test on the bench sheet.

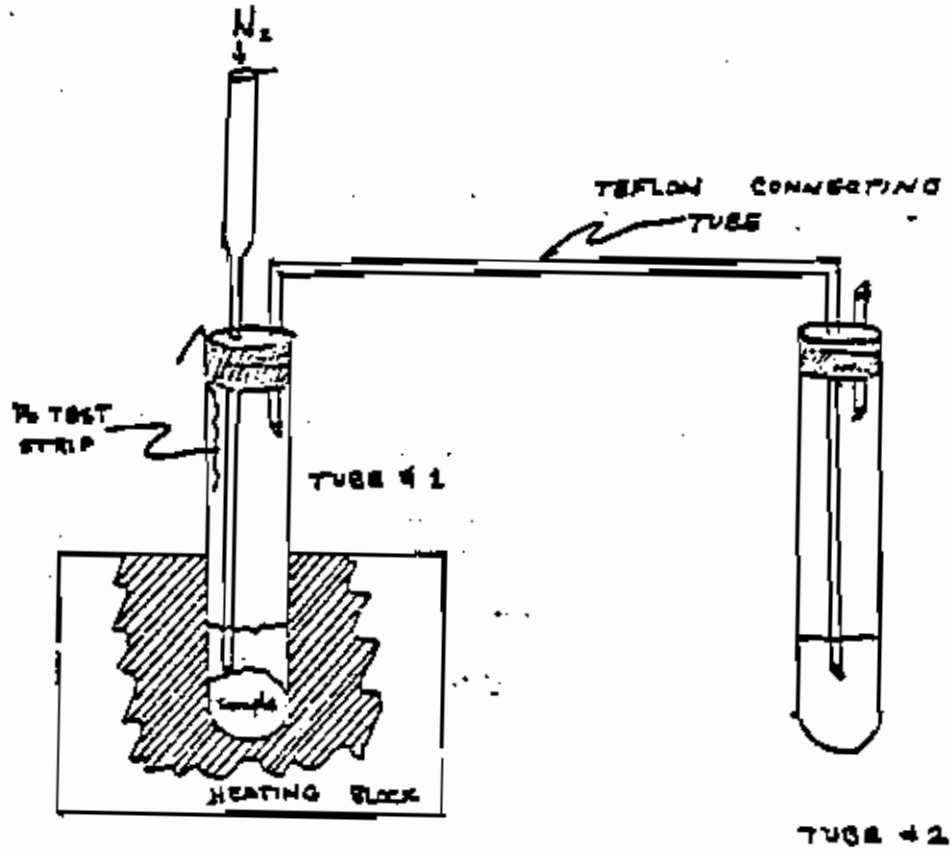


Figure 1. Apparatus for Cyanide and Sulfide Spot Test.

Attachment 4

Method 335.63
Cyanide Determination by Midi Distillation and
Automated Colorimetric Analysis

1. Scope and Application

1.1 This method is applicable to HWDS Solid Phase Samples

1.2 This method is employed only if a positive cyanide spot test is obtained for the solid phase sample. It is also employed if the automated-UV colorimetric analysis of the aqueous phase sample is in question.

2. Summary of Method

2.1 Cyanide is released from its complexes and converted to hydrogen cyanide by means of a reflux-distillation. The hydrogen cyanide gas is drawn by vacuum and absorbed in a solution of sodium hydroxide.

2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride by reaction with chloramine-T at a pH less than 8 without hydrolyzing to cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent and the absorbance is read at 500 nm. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

3. Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample Handling and Preservation

4.1 If a positive spot test was obtained, then one gram of the phase should be placed in the reaction vessel and 10 ml of 0.25 NaOH added to preserve the sample until the test can be started.

4.2 If a positive oxidant spot-test was obtained then there is no need to determine cyanide.

4.3 For solid phase samples, add cadmium nitrate to the absorbing solution of the distillation procedure.

4.4 Samples should be analyzed as rapidly as possible. Samples can be stored if the preservation outlined in 4.1 has been carried out and the preserved sample is stored at 4°C. Seven days is the recommended holding time.

5. Apparatus

5.1 Reflux distillation apparatus consisting of a reaction vessel and condenser plus a gas absorber as shown in figure 1.

5.2 Heating block

5.3 Technicon Auto Analyzer II

5.3.1 Sampler IV

5.3.2 Pump III

5.3.3 Cyanide cartridge

5.3.4 Colorimeter with 50 mm flowcells and 530 or 570 nm filters.

5.3.5 Recorder

5.3.6 Digital Printer

5.4 Plastic Disposable Syringes, 3 ml.

6. Reagents

6.1 Distillation

6.1.1 Sodium Hydroxide Absorbing Solution, 0.25 N-Dissolved 10 g of NaOH in distilled water and dilute to one liter.

6.1.2 Magnesium chloride solution, 51% w/v-Dissolve 510 g of $MgCl_2$-$6H_2O$ in distilled water and dilute to one liter.

6.1.3 Sulfuric Acid - 50% v/v

6.1.4 Sodium Hydroxide Solution, 1.25 N - Dissolve 50 g of NaOH in distilled water and dilute to one liter.

6.2 Standards

6.2.1 Stock Cyanide Solution, 1000mg/l CN - Dissolve 2.51g of KCN and 2g KOH in 1000ml of distilled water. Standardize in accordance with 8.1.

6.2.2 Intermediate Cyanide Standard Solution, 10mg/l CN - Dilute 5ml of the Stock Cyanide Solution (6.2.1) plus 150ml of 1.25N NaOH solution to 500ml with distilled water. Prepare this solution daily.

6.2.3 Working Cyanide Standard Solutions

0-1 ppm CN Calibration Curve

ppm CN	ml #6.2.2	ml #6.1.4	Flask Volume, ml
1.00	10	20	100
0.75	15	40	200
0.50	5	20	100
0.25	5	40	200
0.10	1	20	100

0-0.1 ppm CN - Calibration Curve

ppm CN	ml #6.2.2	ml #6.1.4	Flask Volume, ml
0.100	1	20	100
0.050	2	50	250
0.050	1	40	200
0.025	0.5	40	200
0.010	0.1	20	100

6.2.4 Rhodanine Indicator: Dissolve 20 mg of p-dimethyl-amino-benzal-rhodanine in 100ml of acetone.

6.2.5 Standard Silver Nitrate Solution, 0.0192N - Prepare by crushing approximately 5g $AgNO_3$ crystals and drying to constant weight at 104°C. Weigh out 3.2647g of dried $AgNO_3$, dissolve in distilled water, and dilute to one liter (1ml = 1 mg CN).

6.2.6 Potassium chromate indicator solution. Dissolve 50g K_2CrO_4 in a little distilled water. Add silver nitrate solution until adefinite red precipitate is formed. Let stand 12 hrs., filter, and dilute to one liter with distilled water.

6.2.7 Primary standard sodium chloride, 0.0141 N: Dissolve 824.1mg NaCl (NBS) (dried at 104°C) in distilled water and dilute to one liter.

6.2.8 NaOH Solution, 0.1 N: Dissolve 4g of NaOH in distilled water and dilute to one liter.

6.3 Automated Colrimetric

6.3.1 Phosphate Buffer Solution, 1N - Dissolve 138g of $NaH_2PO_4 \cdot H_2O$ in distilled water and dilute to one liter. Filter before use and store at 4°C.

6.3.2 Chloramine T Solution, 0.4% w/v - Dissolve 0.4g of Chloramine T in distilled water and dilute to 100ml. Prepare fresh daily.

6.3.3 Sample Sodium Hydroxide Wash Solution, 0.25 N - Dissolve 10g of NaOH in distilled water and dilute to one liter.

6.3.4 Pyridine - Barbituric Acid Color Reagent Solution. - Prepare this solution in the hood. Transfer 15g of barbituric acid into a one liter erlenmeyer flask. Add about 100 ml of distilled water and swirl the flask. Add 75 ml of pyridine and mix. Add 15 ml of conc. HCl and mix. Dilute to about 900 ml with distilled water and mix until the barbituric acid is dissolved. Dilute to one liter with distilled water. Store at 4°C.

7. Procedures

7.1 Stock Cyanide Solution Standardization

7.1.1 Fill a 10 ml microburet with the 0.0192 N $AgNO_3$ solution.

7.1.2 Pipet 10 ml of the distilled water into a well washed erlenmeyer flask. Add 100ml of distilled water. Adjust the pH to between 7 and 10 with NaOH or H_2SO_4. Add 1.0 ml of the K_2CrO_4 indicator solution. Titrate with the $Ag(NO_3)$ to a pinkish yellow end point. Be consistent in end-point recognition. Record the ml of titrant used. Titrant three blanks and average the ml of titrant use, this is equal to B.

7.1.3 Titrant three individual 10 ml aliquots of the 0.0141 N NaCl solution in the same manner as the blanks. Average the ml of titrant used, this is equal to A.

7.1.4 Calculate the exact normality of the $Ag(NO_3)$ solution:

$$N\ Ag(NO_3) = \frac{NaCl\ ml}{A-B,\ ml} \times (0.0141\ N)$$

7.1.5 Add 10 ml of distilled water to a well washed erlenmeyer flask. Add 100 ml of 0.1 N NaOH and 0.5 ml of the rhodanine indicator solution. Titrate with the standard Ag (NO_3) titrant to the first change in color from a canary yellow to a salmon hue. Record the ml of titrant used. Titrate three blanks and average the ml of titrant used, this is D.

7.1.6 Titrate three individual 10 ml aliquots of the stock cyanide solution in the same manner on the blanks. Average the ml of titrant used, this is C.

7.1.7 Calculate the concentration of cyanide in the stock solution:

$$mg/l\ CN^- = \frac{(C-D,\ ml)\ N\ Ag\ (NO_3)}{ml\ of\ CN} \times \frac{2\ eq\ CN}{1\ Eq\ AG} \times \frac{26\ g\ CN}{eq} \times 1000\ mg/g$$

7.2 Manual Distillation

7.2.1 Add 50 ml of 0.25 N NaOH to the gas absorbing impinger.

7.2.2 Transfer 1.0 g of solid phase or 1 ml of aqueous phase sample into the 30 ml reaction vessel and add 10 ml of 0.25 N NaOH (section 4.1). Distill one blank, a duplicate, a spiked sample, and an AQC standard for every ten samples. Distill one blank and a standard with each set up.

7.2.3 Add 0.5 ml of the $MgCl.6H_2O$ solution to the reacting vessel ($Mg(OH)_2$ will form).

7.2.4. Connect the reaction vessel, condensor and absorber in place in the laboratory block. Turn on the condenser water to give a flow of 2-4 revolutions/minute on the flow indicator.

7.2.5 Insert a 3ml disposable syringe containing 1.0 ml of 50% v/v H_2SO_4 in the 5/16 in. i.d. tygon tubing above the reaction vessel.

7.2.6 Turn on the vacuum and adjust the needle valve to give a flow of 3 bubbles per second.

7.2.7 Inject the 1.0 ml of 50% H_2SO_4 into the reaction vessel. Turn the heating block on, set at HI and adjust the temperature to 123-125°C.

7.2.8 Heat the solution to boiling, taking care to prevent the solution from backup by periodic adjustment of the vacuum flow rate.

7.2.9 The condenser water flow should be enough to keep the dewpoint about one inch below the gas absorbing outlet. After 2 hours of refluxing turn off the heating block but allow the vacuum to flow for 15 minutes.

7.2.10 Pour the absorbing solution in disposable test tubes, label and cap. This solution is now ready for the colorimetric determination.

7.3 Automated Colorimetric Analyzer

7.3.1 Set up the Auto Anaylzer as shown in Figure 2. Make sure all the waste lines combine together and run a line to the fume hood sink. This is to prevent as much as possible the escape of pyridine vapors in the laboratory. Turn on the faucet.

7.3.2 Turn on the colorimeter, recorder, sampler and printer. Make sure the colorimeter has in place the 580 nm filters (clean these with lense paper and saliva if cloudy or dusty).

7.3.3 Place the sample wash line on the 0.25 N NaOH solution while the other lines are still in distilled water and pump for ten minutes. Then place all of the lines in their appropriate solutions.

7.3.4 Set the printer to 50/hr with a wash time of 6 seconds and a full scale display of 1000. Turn the mode pot on the colorimeter to zero and with the screw pot set the zero on the recorder. At the same time adjust the zero on the printer. Then set the mode pot to full scale and adjust full scale on the recorder and the printer. Recheck the zero and readjust if necessary. Recheck the full scale and readjust if necessary.

7.3.5 Check the bubble pattern of the segmented flow stream and make sure all reagents are being added.

7.3.6 Turn the mode pot on the colorimeter to normal and set the calibration pot to about 1.0. Adjust the zero with the course and fine baseline adjustments.

7.3.7 After obtaining a steady baseline calibrate the system using standards 1.0 through 0.1 ppm. Prepare a Technicon bench sheet. Analyze the control samples and then the distilled samples.

7.3.8 After all analyses are completed turn off the recorder, printer, sampler and colorimeter. Place all lines in distilled water pump for 5 minutes. Then place all lines except the sample wash line in the EDTA-NaOH cleaning solution and pump for 5 minutes. Then place all lines back in distilled and pump for 10 minutes. Clean up any spilled solution and place all reagents back into the cooler. Dump all test tubes and wipe off the sample tray. Turn off the fume hood faucet.

8. Calculations

8.1 Run at least squares data fit of the undistilled standards versus the concentration print out. If the correlation coefficient is greater than 0.99, use the printer concentration for the calculation. If it is less than 0.99, plug all printer concentrations into the calculator and obtain their appropriate values. If it is less than 0.95 then plot the data on graph paper.

8.2 The distilled standards and samples were diluted by a factor of one hundred (0.5 g to 50 ml and 0.5 ml to 50 ml). Therefore their values obtained in 8.1 must be multiplied by one hundred.

8.3 Multiply all distilled values by the standardization value to correct for the fact that the stock cyanide solution is not exactly 1000 mg/l CN^-.

8.4 Average all distilled blanks and subtract this value from all distilled values.

8.5 The cyanide concentration must be reported in ppm CN. Solid phase samples ug/g wet wt. and Aqueous phase samples mg/l.

9. Detection Limit

9.1 The detection limit of the 0-1 ppm method is 0.005 ppm in the absorbing solution.

9.2 The detection limit of the 0.001 ppm method is 0.0005 ppm in the absorbing solution.

10. Quality Control

10.1 All distilled blanks should have a value of less than 0.0010 mg/l.

10.2 The distilled AQC standard should agree to within 10% of the known value.

10.3 A spike and duplicate should be performed every 10th sample. 500 ul of the stock cyanide spiking solution (50 mg/l) should be added as a spike to 1 g of solid sample.

10.4 All duplicated analysis should agree to within 20% at a 0.1 ppm level.

10.5 All spikes greater than 0.1 ppm should be within 20% of the known addition.

10.6 Any of the above out of the control limits indicate the need to reanalyze the samples.

11. Data Reporting

11.1 Fill out the cyanide bench sheet; this will contain all pertinent information.

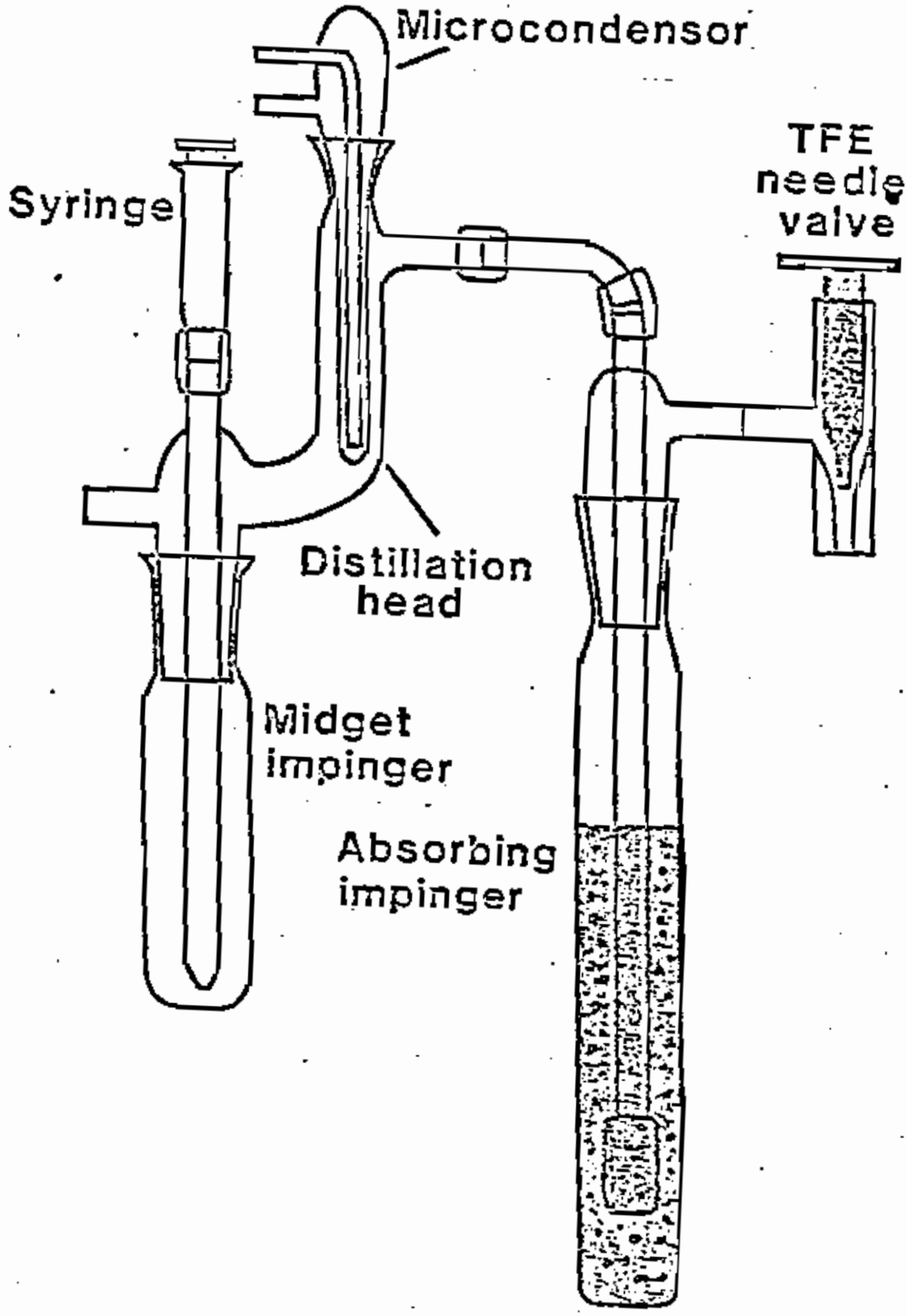

Microcondensor
TFE needle valve
Syringe
Distillation head
Midget impinger
Absorbing impinger

Figure 1

Attachment 5

Method 376.63
Sulfide Determination by Distillation and Colorimetric Analysis for HWDS Solid Phase Samples

1. Scope and Application

1.1 This method is applicable to the determination of sulfides in HWDS Solid Phase samples.

1.2 This method is to be used only after a positive sulfide spot test has been obtained.

2. Summary of Method

2.1 Sulfide is released as hydrogen sulfide from the solid phase sample by the addition of hydrochloric acid. The evolved hydrogen sulfide is swept into a trap filled with zinc acetate by a flow of nitrogen gas. Zinc sulfide forms a precipitate in the trap.

2.2 The zinc sulfide is solubilized in an acidic solution of dimethyl-p-diphenylenediamine and in the presence of ferric chloride forms the dye methylene blue. The color is measured at 670 nm.

3. Sample Handling

3.1 Reagents should be purged with nitrogen before use to reduce dissolved oxygen which can oxidize sulfide to an unmeasurable form.

4. Apparatus

4.1 Distillation apparatus (see Figure 1).

4.2 Temp-Blok Heater or equivalent.

4.3 Thermometer; 0-100°C.

4.4 Spectrophotometer, 670 nm

4.5 1 cm quartz cells.

4.6 N_2 gas tank.

4.7 Matheson 602 rotameter.

5. Reagents

5.1 Standards

5.1.1 Stock sulfide solution, 1000 mg/L S^{2-} - Dissolve 7.50 grams of $Na_2S.9H_2O$ in distilled water and dilute to 1000 mL. Standardize according to 5.1.

5.1.2 Intermediate sulfide standard solution, 100 mg/L S^{2-} - Dilute 10.0 mL of stock sulfide solution to 100.0 mL with 0.25 N NaOH.

5.1.3 Hydrogen Peroxide, 30%.

5.2 Reagents

5.2.1 Zinc acetate, 0.2 N - Dissolve 21.95 g $Zn)Ac.2H_2O$ in distilled water and dilute to one liter.

5.2.2 Aluminum treated hydrochloric acid; 6 N - Add 25 mL of concentrated HCl to 25 mL of distilled water, cool and dissolve 0.1 g of aluminum foil in the diluted acid.

5.2.3 Sodium hydroxide, 1 N - Dissolve 40 grams of NaOH in 800 mL of distilled water, cool and dilute to one liter.

5.2.4 Amine - sulfuric acid stock reagent - Add approximately 25 mL of distilled water to 27 grams of N,N-Dimethyl-p-diphenylene diamine Oxalate. Slowly add while cooling 50 mL concentrated H_2SO_4 to the wet amine. Cool and dilute the solution to 100 mL.

5.2.5 Amine-sulfuric acid working reagent - Dilute 2.5 mL of stock amine-sulfuric acid reagent to 100 mL with 18 N H_2SO_4.

5.2.6 Ferric chloride solution - Dissolve 100 grams of $FeCl_3.6H_2O$ in 40 mL of distilled water.

6. Procedure

6.1 Standardization of stock sulfide standard

6.1.1 Add 1.0 mL of stock sulfide standard to 50 mL of distilled water in a 100 mL volumetric flask.

6.1.2 Add 1 mL of 30% H_2O_2, mix, dilute to volume with distilled water.

6.1.3 Inject the diluted standard into the Ion Chromatograph which is set up for the analysis of sulfate.

6.1.4 Add 1 mL of 30% H_2O_2 to 100 mL of distilled water and analyze this as a blank.

6.2 Distillation (see Figure 1)

6.2.1 Add 1 gram of solid phase sample to the reaction vessel.

6.2.2 Add 1 mL of 1 N NaOH and 3 to 5 mL of distilled water to the reaction vessel.

6.2.3 Fit the distillation head to the reaction vessel and connect the tubing to the nitrogen tank regulator.

6.2.4 Add 50 mL of 0.2 N zinc acetate solution to the trap.

6.2.5 Connect the trap.

6.2.6 Using the regulator and the rotameter, adjust the nitrogen second stage pressure to 5 psi and the flow to 0.15 L/minute. Be sure all valves are open.

6.2.7 Flush the system with nitrogen for ten minutes to reduce dissolved oxygen in the reagents.

6.2.8 During this time turn on the Temp-Block module heater (set for 75°C).

6.2.9 After ten minutes inject 2 mL of aluminum treated b N HCl from the syringe in the distillation head into the reaction vessel.

6.2.10 After the heater has achieved a temperature of 75°C, maintain the distillation for 30 minutes.

6.2.11 After the 30 minute distillation, allow a 10 minute cooling down period.

6.3 Colorimetric Analysis

6.3.1 Inject 100, 50 and 20 ul quantities of 100 mg/L sulfide standard into 50 mL of 0.2 N zinc acetete.

6.3.2 Add 500 uL of amine-sulfuric acid working reagent and then 50 uL of ferric chloride to the standard solutions and the sample.

6.3.3 Add only the color reagents without any sulfide standard addition for the blank.

6.3.4 Allow 30 minutes for color development.

6.3.5 Set the zero on the spectrophotometer with the blank and full-scale with the high standard.

6.3.6 Measure the absorbance of the remaining standards and the sample. The same procedure may also be used with a concentration made.

7. Calculations

7.1 Standardization of stock sulfide standard.

7.1.1 The result from the ion chromatograph in parts per million sulfate should be multiplied times one hundred and then divided by three.

7.2 Calculation of sulfide in sample.

7.2.1 Using least squares linear regression on the absorbances obtained from the calibration standards calculate the sample results in ug.

7.2.2 If any dilution was made on the trap solution after the distillation and color development to bring the absorbance value for tne sample within the working range, multiply the sample value in ug by the dilution factor.

7.2.3 Divide the sample value in ug by the sample wet weight (in grams) used in the procedure. Report results as ug/g wet weight.

8. Quality Control

8.1 Distilled water blanks should be run each time a spiked sample is analyzed.

8.2 Spiked sample analysis will be performed every tenth sample. Spikes will consist of addition of 100 ul of 50 mg/L S^{2-} standard to the reaction vessel containing the solid phase sample before distillation begins. Percent recovery should be within 20% of 100%.

8.3 Duplicate distillation and analysis will be performed every tenth sample. Results should agree within 20% of the mean value.

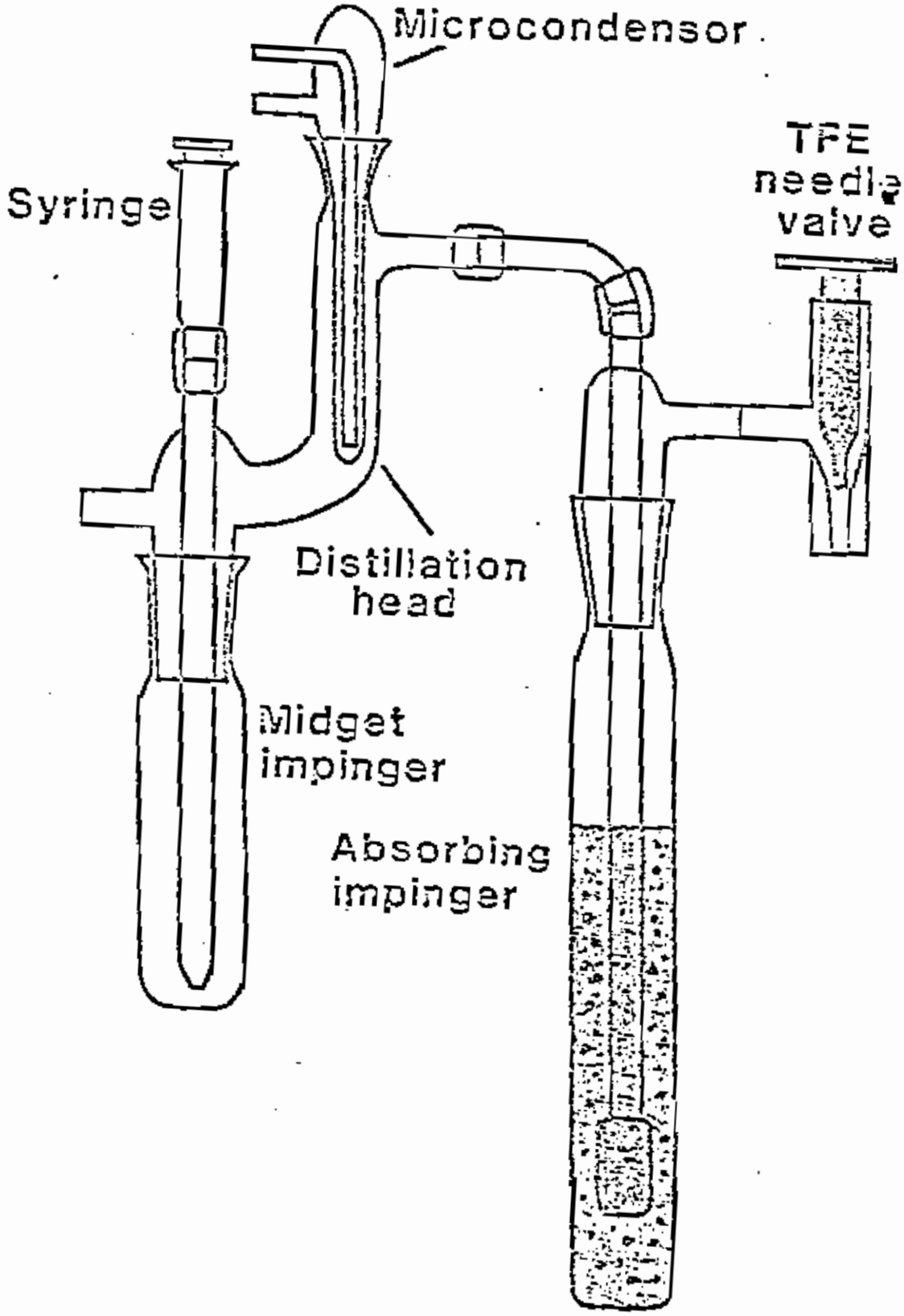

Microcondensor
TFE needle valve
Syringe
Distillation head
Midget impinger
Absorbing impinger

Figure 1

EXHIBIT E

QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

GENERAL QA/QC CONSIDERATIONS

Standard laboratory practices for laboratory cleanliness as apply to glassware and apparatus must be adhered to. Laboratory practices with regard to reagents, solvents, and gases should also be adhered to. For additional guidelines regarding these general laboratory procedures, please see Sections 4 and 5 of the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1979.

QUALITY ASSURANCE REQUIREMENTS

The quality assurance/quality control (QA/QC) procedures defined below must be used by the Contractor when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in the methods in Exhibir D, the Contractnr must also follow these procedures. The cost of performing ell QA/QC procedures specified in this Statement nf Work is included in the price of performing the bid lot.

Tha purpose of thie document is to provide e uniform sat of procedures for tbe analysis of inorganic conscituents of samples, documentetion of methode and their performance during a aurvey, and verificetion of the sample date generaced. The program will also assisc laboretory personnel in recalling and defending tbeir actions under cross examination if required to present nourt testimony in enforcement cese litigetion.

The prime function of the QA/QC program outlined bere ia tha definition of procedurea for the evaluation and documentation of aampling end analytical methodologies and the reduction and reporting of data. The objective ie to provide a uniform besia for aample collection end handling, instrument and methoda maintenance, performanne evaluation, and analytical dara gethering and reporting. Although it ia impossible to address all analytical situations in one document, the epproach taken here is to define minimum requirements for all major steps relevant to any analysis. In many instances where methodologies are available, specific quality control procedures are incorporated into the method documentation. Ideally, samples involved in enforcement actione are analyzed only after the methods have met the minimum performance and documentation requirements described in this document.

The Contractor must participate in the Laboratory Intercomparison Study Program run by EPA, EMSL-Las Vegas. The Contractor can expect to analyze two samples per three-month contract period for this program.

The Contractor must record all QC data by perameter in tabular format. (See QC Forms 11, 1II, IV, V and Vl in Exhibit B.)

This aection outlines the miminum QA/QC operatione necessary to satisfy the analytical requirements of the contract. Tbe following QA/QC operations must be performed during each enalyrical run:

1. Initial Calibration and Calibration Verification

2. Continuing Calibration Verification

3. Preparation Blank Analysis

4. Interference Check Sample Analysis

5. Matrix Spike Analysis

6. Duplicate Sample Analysis

1. Initial Calibration and Calibration Verification

Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Exhibit D.

After the ICP, AA and classical inorganic systems have been calibrated, the accuracy of the initial calibrating solutions shall be documented for every analyte by the analysis of EPA Quality Control Solutions (available from EPA, Telephone 513-684-7325) or, for certified trace elements, NBS SRM 1643a (available from the National Bureau of Standards, Telephone 301-921-2045).

Where a certified solution of an analyte is not available, analyses of the calibrating standard at a dilution other than that used for calibration shall be conducted (e.g., boron, tin and sulfide are not currently present in EPA Quality Control Samples). When measurements for the certified components differ statistically from the accepted value (i.e., exceed the control limits of Table 1) and the discrepancy cannot be resolved by using freshly prepared, properly diluted and preserved calibrating standards, the concentration for the calibrating standard stock solution shall be adjusted to result in acceptable measurements for the certified solution components.

The values for the initial and subsequent calibration verifications shall be recorded on Forms III to VI (see Exhibit B) for ICAP, AA, and classical inorganic analyses, as indicated.

Before any field samples are analyzed under this contract (but not more than 30 days before such analyses commence), the instrumental detection limits (in ug/L) must be documented and shall meet the levels specified in Exhibit C. The instrumental detection limits (in µg/L) shall be determined by multiplying by 3, the standard deviation obtained for the appropriate calibration blank solution from three (3) nonconsecutive analysis days with 10 consecutive measurements per day. Each day analyses are conducted the instrumental sensitivity (i.e., absorbance for atomic absorption and gain values for inductively coupled plasma for a known amount of analyte) must be recorded and included with the appropriate QC report.

Fresh calibrating solution dilutions for trace elements shall be prepared monthly (unless contractor data is available to demonstrate longer stability) and before each set of diluted calibration standards is consumed. In order to maintain traceability to the reference standards old and new sets of

TABLE 1. CONTROL LIMITS FOR INORGANIC ANALYSES

Analysis Method	Inorganic Species	% of True Value (EPA Set) Low Limit	High Limit
ICP Spectroscopy	Aluminum	85	115
	Barium	84	116
	Beryllium	87	113
	Boron	84	116
	Chromium	88	112
	Cobalt	78	122
	Copper	83	117
	Iron	88	112
	Manganese	90	110
	Nickel	89	111
	Silver	80	120
	Vanadium	90	110
	Zinc	75	125
Atomic Absorption Spectrometry	Arsenic	86	114
	Antimony	85	115
	Cadmium	80	120
	Lead	78	122
	Mercury	80	115
	Selenium	85	115
	Thallium	88	112
	Tin	75	125
Other Inorganic Analyses	Ammonia	80	120
	Cyanide	80	120
	Sulfide	85	115

calibration standards must agree (based on conventional t-test analysis) using data from five (5) alternating measurements on the old and new diluted standards before a new set of calibrating standards is accepted for use.

A calibration blank is analyzed each time the instrument is calibrated. The results for the calibration blank solution shall be recorded on Forms III to VI for ICP, AA and classical inorganic analyses, as indicated.

2. Continuing Calibration Verification

To assure calibration accuracy during an analysis run, one of the following standards is analysed for each analyte after every 10 samples:

1. EPA Quality Control Solutions

2. NBS SRM 1643a

3. A contractor-prepared standard solution

If the deviation is greater than the Control Limits specified in Table 1, corrective action such as recalibration must be taken and the preceding 10 samples reanalyzed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on Forms III to VI (see Exhibit B) for ICP, AA and classical inorganic analyses, as indicated.

3. Preparation Blank Analysis

At least one preparation blank (consisting of the method required reagents processed through each analytical procedure) must be analyzed with each case or for each 20 samples, whichever is more frequent. This blank is used in all analyses to ascertain whether sample concentrations reflect contamination. If an inorganic species of interest is detected in the blank, the blank value is utilized in the sample calculation according to the following:

1. If the concentration in the blank is less than the required detection limit (Exhibit C), no correction of sample results is performed.

2. If the concentration in the blank is greater than the required detection limit and is less than or equal to one-half the concentration detected in a sample, subtract the concentration in the blank from the concentration in the sample. Record on the data form the corrected value (when it exceeds the detection limit) and indicate that this has been done by placing a "C" adjacent to the recorded result.

3. If the concentration in the blank is greater than the detection limit, and if the blank concentration is greater than one-half the concentration detected in a sample, accurate correction is not considered reliable, and the analyte should be reported as "ND" with a "B" adjacent to it on the data sheet. Efforts should be made to keep blank values as low as possible.

The values for the preperation blank shall be recorded on Forms III to VI for ICP, AA, and classicial inorganic analyses, as indicated.

4. ICP Interference Check Sample Analysis

The ICP Interferenne Check Sample allows the analyst to verify inter-element and background correction factors on a regular basis. It should be analyzed at the beginning and end of a sample run (minimum of twice per working shift). The ICP Interference Check Sample is available from EPA (telephone 513-684-7325). See Table 3 for example interferent and analyte elemental concentrations used for interference measurements.

Results of interference check sample analyees should be recorded and so labeled under Section II of Form III.

5. Spiked Sample Analysis

The spiked sample analysis is designed to provide information about the affect of the sample matrix on the measurement methodology. The spike is added after the extraction but prior to any distillation steps (e.g., CN^- and NH_3). Spiking the sample prior to preparation can be complicated by absorption characteristics of the waste that can confound interpretation of the renovery data, and it is thus added as stated above. At least one spiked sample analysis shall be performed on each group of samples of a similar matrix for each case of samples received or for each 20 samples, whichever is more frequent.* The analyte spike should be added to obrain twice the endogenous level (ar a minimum of ten times the detection limit) for each element analyzed. If the spike recovery is nor within the limits given in Table 2, the net response fur the sample spike shall be used as a single point method of addition calibration for the spiked sample.* Individual componant percenc recoveries are calculated as follows:

$$\%\text{Recovery} = \frac{(SSR-SR)}{SA} \times 100$$

Where SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

*EPA may require standard addition analysis (by means of spike recovery tests) for additional samples of the same waste type analyzed, on request, and pay for same.

TABLE 2. SPIKED SAMPLE RECOVERY LIMITS

Analysis Method	Inorganic Species	% of True Value (EPA Set)	
		Low Limit	High Limit
ICP Spectroscopy	Aluminum	80	120
	Barium	80	120
	Beryllium	80	120
	Boron	80	120
	Chromium	80	120
	Cobalt	80	120
	Copper	80	120
	Iron	80	120
	Manganese	80	120
	Nickel	80	120
	Silver	80	120
	Vanadium	80	120
	Zinc	80	120
Atomic Absorption Spectrometry	Arsenic	75	125
	Antimony	75	125
	Cadmium	75	125
	Lead	75	125
	Mercury	75	125
	Selenium	75	125
	Thallium	75	125
	Tin	75	125
Other Inorganic Analyses	Ammonia	80	120
	Cyanide	80	120
	Sulfide	80	120

TABLE 3. EXAMPLE INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR INTERFERENCE MEASUREMENTS

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Ti	10		
V	1		
Zn	10		

Samples analyzed by the standard addition method are marked on the data sheets with the letter s. The spiked sample results shall be reported on Forms II to VI for ICP, AA and classical inorganic analyses, as indicated.

6. Duplicate Sample Analysis

At least one duplicate sample analysis shall be performed on each group of samples of a similar matrix for each case of samples received or for each 20 samples, whichever is more frequent.* The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

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

The results of the duplicate analysis must be reported on Forms II to VI. The percent difference data will be used by EPA to evaluate the long term precision of the method.

*EPA may require additional duplicates be analyzed, on request, for which contractor will be paid.

II. LABORATORY AUDIT PROCEDURES

This document outlines the procedures which will be used by the EPA Project Officer or his authorized representative in order to conduct a successful laboratory audit with respect to the analysis of water, soil, sludge or sediment samples for inorganic priority pollutants and other inorganic species. The audit process incorporates two major steps: (1) analysis of intercomparison study samples; and (2) on-site inspection of the laboratory to verify continuity of personnel, instrumentation and quality control functions. The following is a description of these two steps.

1. Intercomparison Study Samples

Two intercomparison study samples will be sent to each contract laboratory on a quarterly basis to verify the laboratory's continuing ability to produce acceptable analytical results. The samples will be sent in such a way as to be indistinguishable from other samples currently being processed and reported by the laboratory, to assure that they are processed in a routine manner by laboratory personnel. Intercomparison Study Samples will contain a representative array of metals and inorganic compounds that will normally be the subject of analysis under this contract.

When the intercomparison study sample data are received by EPA, results are scored using the Sample Data Scoring Sheet shown in Table 4. A score of 160 points or more is evidence of acceptable performance. If a score of less than 160 points is obtained, the laboratory is not performing acceptably and they shall be so notified immediately. If a laboratory is so notified, they will be provided with an additional aliquot of the appropriate study sample they just failed to analyze acceptably, told what their problem was, and instructed to reanalyze the sample. If the laboratory fails to solve their problems immediately, they must discontinue analysis of samples until the problem has been corrected and demonstrated through acceptable analysis of a different set of study samples.

TABLE 4. INTERCOMPARISON SAMPLE DATA SCORING (Maximum = 200 points)

Laboratory _____ Date _____

Scoring: Sample Set 1 ____ Sample Set 2 ____ Total Score _____

Sample Set 1	Points
I. Identifications	
A. Hazardous Materials-Metals (Maximum of 20 Points)	_____
1. All metals detected.	20
2. One not detected.	15
3. Two not detected.	10
4. More than two not detected.	0
B. Non-Metal Inorganics (Maximum of 20 Points)	_____
1. All non-metal inorganics detected.	20
2. One not detected.	15
3. Two not detected.	10
4. More than two not detected.	0
II. Quantitation	
A. Hazardous Materials-Metals (Maximum of 20 Points)	_____
1. All metals within EPA acceptance criteria window.	20
2. One outside acceptance criteria window.	15
3. Two outside acceptance criteria window.	10
4. More than two outside acceptance criteria window.	0
B. Non-Metal Inorganics (Maximum of 20 Points)	_____
1. All non-metal inorganics within EPA acceptance criteria window.	20
2. One outside acceptance criteria window.	15
3. Two outside acceptance criteria window.	10
4. More than two outside acceptance criteria window.	0
C. Percent Differences (Maximum of 10 Points)	_____
1. All within EPA acceptance criteria window.	10
2. One outside acceptance criteria window.	8
3. Two outside acceptance criteria window.	5
4. More than two outside acceptance criteria window.	0
Total/Sample Set 1 (Maximum = 90 Points)	_____

Sample Set 2

	Points
I. Identifications	
A. Analyte Metals (Maximum of 20 Points)	_____
1. All analyte metals detected.	20
2. One not detected.	15
3. Two not detected.	10
4. More than two not detected.	0
B. Interference Metals (Maximum of 10 Points)	_____
1. All interference metals detected.	10
2. One not detected.	8
3. Two not detected.	5
4. More than two not detected.	0
II. Quantitation	
A. Analyte Metals (Maximum of 20 Points)	_____
1. All analyte metals within EPA acceptance criteria window.	20
2. One outside acceptance criteria window.	15
3. Two outside acceptance criteria window.	10
4. More than two outside acceptance criteria window.	0
B. Interference Metals (Maximum of 10 Points)	_____
1. All interference metals within EPA acceptance criteria window.	10
2. One outside acceptance criteria window.	8
3. More than one outside acceptance criteria window.	0
III. Quality Assurance Data	
A. Hazardous Materials-Metal Spikes (Maximum of 20 Points)	_____
1. All metal spikes within EPA acceptance criteria window.	20
2. One outside acceptance criteria window.	15
3. Two outside acceptance criteria window.	10
4. More than two outside acceptance criteria window.	0

Sample Set 2 (continued)

IV. Reagent Blank Analysis

A. Hazardous Materials-Metals (Maximum of 10 Points) _____

1. None reported in reagent blank.	10
2. None reported at 50% greater than their detection limits.	8
3. One-two reported at 50% greater than their detection limits.	5
4. More than two reported at 50% greater than their detection limits.	0

B. Non-Metal Inorganics (Maximum of 10 Points) _____

1. None reported in reagent blank.	10
2. None reported at 50% greater than their detection limits.	8
3. One-two reported at 50% greater than their detection limits.	5
4. More than two reported at 50% greater than their detection limits.	0

V. Reporting and Deliverables (Maximum of 10 Points) _____

1. Data results supplied in acceptable format.	3
2. Quality Assurance/Quality Control data supplied in acceptable format.	4
3. Tabulated instrument detection limits supplied.	3

Total/Sample Set 2
(Maximum = 110 Points) _____

Total Score/Sample Sets 1 and 2
(Maximum = 200 Points) _____

2. ON-SITE LABORATORY INSPECTION

An On-site Laboratory Inspection is performed to verify that the laboratory is maintaining the necessary minimum level in instrumentation and required levels of experience in personnel committed to the project, and that the necessary quality control activities are being carried out. However, it also serves as a mechanism for discussing weaknesses identified through Intercomparison Study Sample analysis.

The following describes the protocol which is adhered to during an on-site laboratory inspection. Included is a Site Inspection Score Sheet (SISS) that will be completed during the site visit.

2.1 Event Sequence

I. Meeting with Laboratory Manager and Project Manager

A. Introduction
B. Discuss purpose of visit
C. Discuss any problems with sample data submitted by lab

II. Verification of Personnel

A. Review Section I of Score Sheet (see Table 5) and identify any changes in personnel compared with the most recent SISS. If changes have been made, verify experience. If more than one individual satisfies the minimum requirements, identify the most highly committed to the project.

B. Check the point total; if less than the maximum number of points is obtained, the lab does not satisfy the minimum requirements and is not considered qualified to continue performing analyses until the problem has been corrected.

III. Verification of Instrumentation

A. Review Section II of SISS to identify any changes in equipment committed to this project. If any changes have been made, verify new equipment acceptability for the project. If more than one instrument is available which satisfies the minimum requirements, identify the one most highly committed to the project.

B. Check the point total; if less than the maximum number of points is obtained, the laboratory does not satisfy the minimum requirements and is not considered qualified to continue performing analyses until the problem has been corrected.

IV. Quality Control Procedures

A. Walk through the laboratory following the steps that would be followed by a sample. Have the "tour guide" point out:

1. How samples and extracts are received, maintained, and documented.

2. Sample and extract storage areas (note available space).

3. Steps taken to assure cleanliness and avoid contamination.

4. Security measures, document and sample control.

5. Written standard operating procedures.

6. Instrument records and logbooks.

7. Data control system.

8. Management review of data.

B. Go through Section III of the SISS to verify that the laboratory has acceptably corrected all previously identified problems. Calculate the point total. If less than the maximum number of points is obtained, the lab does not satisfy the minimum requirements and is not considered qualified to continue performing analyses until problems have been corrected.

V. Identification of New Problems

A. Discuss any weaknesses identified in the Intercomparison Study Sample analyses and reports.

B. Discuss any weaknesses identified in this site inspection.

C. Get concurrence by project manager (person identified in Section I.A. of the SISS) that all weaknesses will be corrected. Point out that any weak areas in the facility which have been identified in this site inspection will have corrective actions verified before the next audit. Weaknesses not corrected may be cause for penalties or contract termination.

TABLE 5. SITE INSPECTION SCORE SHEET

Laboratory _____ Location _____ Date _____

Reason for visit:

Evaluation

	Name	Organization	Signature
1.			
2.			
3.			
4.			

I.	Laboratory Personnel Committed to Project	Points
A.	Laboratory or Project Manager (individual responsible for overall technical effort): Name _____	1
B.	Inductively Coupled Plasma Emission Spectroscopist: Name _____	1
C.	Flameless Atomic Absorption Spectroscopist: Name _____	1
D.	Inorganic Compounds Analyst (prepares ICP and AA samples): Name _____ Experience (1 year minimum requirement)	1
E.	Sample Extraction Expert: Name _____ Experience (3 months minimum requirement)	1
F.	Classical Inorganic Techniques Analyst: Name _____ Experience (6 months minimum requirement in sulfide, cyanide and ammonia)	1

(continued)

TABLE 5. (Continued)

	Points
II. Laboratory Equipment	
A. Inductively Coupled Plasma (ICP) Spectrometer committed to this project and operational.	1
B. Flameless Atomic Absorption Spectrometer committed to this project and operational.	1
Cell and reduction assembly for cold vapor mercury determinations.	1
C. pH and ion selective meters.	1
D. uv-visible spectrophotometer.	1
III. Quality Control Procedures	
A. Sample Control	
1. Sample receipt, storage and sample extract accounting procedure exists and is in use.	1
2. There is one responsible individual for sample control (Name _____).	1
3. Samples and sample extracts are kept in a secure (locked) area when not in use.	1
B. Analysis Control	
1. All individuals working on the project have written protocols describing their required activities.	1
2. There is a logbook for each instrument for recording performance information such as calibration data and service activities.	1
3. Facility is designed for trace inorganic analyses of hazardous wastes.	1
a. Adequate ventilation is provided in sample preparation and analysis.	1
b. The ICP spectrometer is properly vented.	1
c. The atomic absorption spectrometer is properly vented.	1
d. Adequate procedures exist for disposal of waste liquids from the ICP and AA spectrometer.	1

(continued)

TABLE 5. (Continued)

	Points
4. Sufficient 4°C storage space for samples and sample extracts (1 ft^2/sample/month).	1
C. Document Control	
1. Every individual participating in this project has a notebook for maintaining detailed records.	1
2. There is a single individual responsible for maintaining all records and documents (Name _____).	1
D. Good laboratory practices and standard operating procedures (SOP's) are documented. (Examples of SOP's would be procedures for cleaning glassware and calibrating instruments.)	1

TOTAL SCORE _____

(If less than 25 points, discuss each problem with person identified in I.A. as described in IV below.)

IV. Conclusion

A. Previously Identified Problems.

All previously identifed problems have been corrected.

Yes _____ No _____ (Check one)

If the answer is "No," the laboratory is not performing acceptably and must discontinue sample analysis under this contract until problems are corrected.

B. Intercomparison Study Sample data reporting problems have been discussed and any required corrective actions have been committed to by the individual identified in Section I.A. of this form.

Signature of Project Manager (identified in Section I.A).

_____

EXHIBIT F

SAMPLE PRESERVATION AND HOLDING TIMES

REQUIREMENTS FOR SAMPLE CONTAINERS, PRESERVATION PROCEDURES AND MAXIMUM HOLDING TIMES OF SAMPLES

Measurement[a]		Container[b]	Preservative[c]	Maximum Holding Time[d]
1	Acidity	P,G	Cool, 4°C	14 days
2	Alkalinity	P,G	Cool, 4°C	14 days
3	Ammonia	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
	BACTERIA			
4-7	Coliform, fecal and total	P,G	Cool, 4°C 0.008% $Na_2S_2O_3$	6 hours
8	Fecal streptococci	P,G	Cool, 4°C 0.008% $Na_2S_2O_3$	6 hours
9	Biochemical oxygen demand	P,G	Cool, 4°C	48 hours
10	Bromide	P,G	None required	28 days
11	Chemical oxygen demand	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
12	Chloride	P,G	None required	28 days
13	Chlorine, total residual	P,G	Determine on-site	2 hours
14	Color	P,G	Cool, 4°C	48 hours
15-16	Cyanide, total and amenable to chlorination	P,G	Cool, 4°C NaOH to pH>12 0.008% $Na_2S_2O_3$	14 days

(continued)

REQUIREMENTS FOR SAMPLE CONTAINERS, PRESERVATION PROCEDURES AND MAXIMUM HOLDING TIMES OF SAMPLES

Measurement[a]		Container[b]	Preservative[c]	Maximum Holding Time[d]
17	Dissolved oxygen			
	Probe	G bottle & top	Determine on site	1 hour
	Winkler	G bottle & top	Fix on site	8 hours
18	Fluoride	P	None Required	28 days
19	Hardness	P,G	HNO_3 to pH<2	6 months
28	Hydrogen ion (pH)	P,G	Determine on site	2 hours
21 & 91	Kjeldahl and organic nitrogen	P,G	Cool; 4°C H_2SO_4 to pH<2	28 days
	METALS[e]			
38-39	Chromium VI	P,G	Cool, 4°C	48 hours
56-57	Mercury	P,G	HNO_3 to pH<2 0.05% $K_2Cr_2O_7$	28 days
22-85	Metals except above	P,G	HNO_3 to pH<2	6 months
06	Nitrate	P,G	Cool, 4°C	48 hours
07	Nitrate-nitrite	P,G	Cool 4°C H_2SO_4 to pH<2	20 days
08	Nitrite	P,G	Cool, 4°C	48 hours

(continued)

REQUIREMENTS FOR SAMPLE CONTAINERS, PRESERVATION PROCEDURES AND MAXIMUM HOLDING TIMES OF SAMPLES

Measurement[a]		Container[b]	Preservative[c]	Maximum Holding Time[d]
17	Dissolved oxygen			
	Probe	G bottle & top	Determine on site	1 hour
	Winkler	G bottle & top	Fix on site	8 hours
18	Fluoride	P	None Required	28 days
19	Hardness	P,G	HNO_3 to pH<2	6 months
20	Hydrogen ion (pH)	P,G	Determine on site	2 hours
21 & 91	Kjeldahl and organic nitrogen	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
	METALS[e]			
38-39	Chromium VI	P,G	Cool, 4°C	48 hours
56-57	Mercury	P,G	HNO_3 to pH<2 0.05% $K_2Cr_2O_7$	28 days
22-85	Metals except above	P,G	HNO_3 to pH<2	6 months
86	Nitrate	P,G	Cool, 4°C	48 hours
87	Nitrate-nitrite	P,G	Cool 4°C H_2SO_4 to pH<2	28 days
88	Nitrite	P,G	Cool, 4°C	48 hours

(continued)

REQUIREMENTS FOR SAMPLE CONTAINERS, PRESERVATION PROCEDURES AND MAXIMUM HOLDING TIMES OF SAMPLES

	Measurement[a]	Container[b]	Preservative[c]	Maximum Holding Time[d]
89	Oil and Grease	G	Cool, 4°C H_2SO_4 to pH<2	28 days
	ORGANIC COMPOUNDS[f]			
	Extractables (including phthalates, nitrosamines organochlorine pesticides, PCB's, nitroaromatics, isophorone, polynuclear aromatic hydrocarbons, haloethers, chlorinated hydrocarbons and TCDD)	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$	7 days (until extraction) 30 days (after extraction)
	Extractables (phenols)	G, teflon-lined cap	Cool, 4°C H_2SO_4 to pH<2 0.008% $Na_2S_2O_3$	7 days (until extraction) 30 days (after extraction)
	Purgeables (Halocarbons and Aromatics)	G, teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$	14 days
	Purgeables (Acrolein and Acrylonitrile)	G, teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$	3 days
90	Organic Carbon	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
92	Orthophosphate	P,G	Filter on site Cool, 4°C	48 hours
93	Phenols	P,G	Cool, 4°C H_2SO to pH<2	28 days

(continued)

REQUIREMENTS FOR SAMPLE CONTAINERS, PRESERVATION PROCEDURES AND MAXIMUM HOLDING TIMES OF SAMPLES

Measurement[a]		Container[b]	Preservative[c]	Holding Time[d]
94	Phosphorus (elemental)	G	Cool, 4°C	48 hours
95	Phosphorus, total	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
	RADIOLOGICAL			
96-100	Alpha, Beta and radium	P,G	HNO_3 to pH<2	6 months
101	Residue, total	P,G	Cool, 4°C	14 days
102	Residue, filterable	P,G	Cool, 4°C	14 days
103	Residue, nonfilterable	P,G	Cool, 4°C	7 days
104	Residue, settleable	P,G	Cool, 4°C	7 days
105	Residue, volatile	P,G	Cool, 4°C	7 days
71	Silica	P	Cool, 4°C	28 days
T06	Specific conductance	P,G	Cool, 4°C	28 days
T07	Sulfate	P,G	Cool, 4°C	28 days
108	Sulfide	P,G	Cool, 4°C Zinc Acetate	28 days
109	Sulfite	P,G	Cool, 4°C	48 hours
110	Surfactants	P,G	Cool, 4°C	48 hours

(continued)

REQUIREMENTS FOR SAMPLE CONTAINERS, PRESERVATION PROCEDURES AND MAXIMUM HOLDING TIMES OF SAMPLES

Measurement[a]		Container[b]	Preservative[c]	Maximum Holding Time[d]
111	Temperature	P,G	Determine on site	Immediately
112	Turbidity	P,G	Cool, 4°C	48 hours

a Parameter numbers refer to Table 1.
b Polyethylene (P) or Glass (G).
c Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection, if possible. Aliquots of the composite, which would require multiple preservatives, should be preserved only by maintaining at 4°C until compositing and sample splitting is completed.
d Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time.

Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample stability.
e Samples should be filtered immediately on-site before adding preservative for dissolved metals.
f Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific organic compounds.

EXHIBIT G

CHAIN-OF-CUSTODY AND DOCUMENT CONTROL PROCEDURES

NOTE

The Contractor shall not deviate from the procedures described herein without the prior written approval of the Contracting Officer: Provided, that the Contracting Officer may retify in writing such deviation and such ratification shall constitute the approval required herein.

Specifications for Chain-of-Custody and Document Control Procedures

The contractor must have written standard operating procedures (SOP) for receipt of samples, maintenance of custody, tracking the analysis of samples and assembly of completed data. These procedures are necessary to ensure that analytical data collected under this contract are acceptable for use in EPA enforcement case preparations and litigation. The contractors SOP's shall provide mechanisms and documentation to meet each of the following specifications and shall be used by EPA for the basis for laboratory evidence audits.

1. The contractor shall have a designated sample custodian responsible for receipt of the samples.

2. The contractor shall have written SOP's for receiving and logging in of the samples. The procedures shall include documentation of the sample condition, maintenance of custody and sample security and documentation of verification of sample tag information against custody records.

3. The contractor shall have written SOP's for maintenance of the security of the samples after log in and shall demonstrate security of the sample storage and laboratory areas.

4. The contractor shall have written SOP's for tracking the work performed on any particular sample. The tracking system shall include standard data logging formats, logbook entry procedures and a means of controlling logbook pages, computer printouts, chromatograph tracings and other written or printed documents relevant to the samples. Loghooks, printed forms or other written documentation must be available to describe the work performed in each of the following steges of analysis:

   - Sample receipt
   - Sample extraction/preparation
   - ICAP analysis
   - Flameless and cold vapor AA analysis
   - Inorganics analysis
   - Data reduction
   - Data reporting

5. The contractor shall have written SOP's for organization and assembly of all documents relating to each EPA case. Documents shall be filed on a case specific basis. The procedures must ensure that all documents including logbook pages, sample tracking records, measurement readout records, computer printouts, raw data summaries, correspondence and any other written documents having reference to the case are compiled in one location for submission to EPA. The system must include a document numbering and inventory procedure.

6. Document control and chain-of-custody records include but are not limited to: sample tags, custody records, sample tracking records, analysts logbook pages, bench sheets, measurement readout records, extraction and analysis chronicles, computer printouts, raw data summaries, instrument logbook pages, correspondence, and the document inventory.

Hazardous Waste Disposal Site
Contract Analytical Support
Chain-of-Custody and Document Control Procedures

Sample Control

A sample is physical evidence collected from a facility or from the environment. An essential part of this investigations effort is the control of the evidence gathered. To accomplish this, the following chain-of-custody and document control procedures have been established.

Sample Identification

Each sample bottle shall be labeled with a tag containing the sample number and sample description to identify the contents of the bottle. Additionally, the sample number shall be marked on the outside of any special packaging container to facilitate identification. Typical sample tags are shown in Figure 1.

Chain-of-Custody Procedures

Because of the nature of the data being collected, the possession of samples must be traceable from the time the samples are collected until they are introduced as evidence in legal proceedings. To maintain and document sample custody, the chain-of-custody procedures described here are followed.

A sample is under custody if:

1. It is in your actual possession, or

2. It is in your view, after being in your physical possession, or

3. It was in your possession and then you locked or sealed it up to prevent tampering, or

4. It is in a secure area.

To assure custody of samples during transport and shipping, each sample within a packing container is recorded on a chain-of-custody record shown in Figure 2. Each sample number is recorded and the number of containers shipped is recorded on the sheets. Also record the other information regarding the project, samples (or shipper if returning empty bottles), method of shipment and remember to sign and date the sheet. The original custody sheet is then placed inside the package (protected from damage) and the package sealed.

Sample containers, shipping boxes, coolers or other packages may be sealed by using the seal shown in Figure 3. The seal must be placed so the container cannot be opened without breaking the seal.

Upon receipt of samples in custody, inspect the package and note any damage to the sealing tape or custody seals. Note on the custody record or other logbook that the seals or locks were intact upon receipt if no tampering or damage appears to have occurred. Open the package and verify that each item listed on the sheet is present and correctly identified. If all data and samples are correct, sign and date the "received by Laboratory by" box. In the event errors are noted, record the discrepancies in the remarks column (initial and date each comment) then sign the chain-of-custody record. Report discrepancies to the Sample Management Office for remedies.

Laboratory Document Control

The goal of the Document Control Program is to assure that all documents for a specified case (group of samples) will be accounted for when the project is completed. The program includes a document numbering and inventory procedure for preparation of the specified documentation packages for each case.

Logbooks

All observations and results recorded by the laboratory but not on preprinted data sheets are entered into permanent laboratory logbooks. Data recorded are referenced with the case number, date and analyst's signature at the top of the page. Data from only one case are recorded per page. When all the data from a case is compiled, copies of <u>all</u> logbook entries must be included in the documentation package.

Instrument logs are also limited to one case per page with the case number recorded at the top of each page. Copies of these logs must also be included in the final documentation package.

Corrections to Documentation

All documentation in logbooks and other documents shall be in ink. If an error is made in a logbook assigned to one individual, that person should make corrections simply by crossing a line through the error and entering the correct information. Changes made subsequently are dated and initialed. Corrections made to other data records or non-personal logbooks are made by crossing a single line through the error, entering the correct information and initialing and dating the correction.

Consistency of Documentation

Before releasing analytical results, the laboratory assembles and cross checks the information on sample tags, custody records, lab bench sheets, personal

and instrument logs and other relevant data to ensure that data pertaining to each particular sample or case is consistent throughout the record.

Document Numbering and Inventory Procedure

In order to provide document accountability of the completed analysis records, each item in a case is inventoried and assigned a serialized number and an identifier associating it to the case and Region.

Case # - Region - Serialized number

For example - 75-2-0240

All documents relevant to each case including: logbook pages, bench sheets, mass spectra, chromatograms, custody records, library search results, etc., are inventoried. Each data generator (analyst) is responsible for ensuring that all documents generated are placed in the file for inventory and return to EPA. Figure 4 is an example of a document inventory.

Confidential Information

Any samples or information received with a request of confidentiality is handled as "confidential." A separate, locked file is maintained and segregated from other nonconfidential information. Data generated from confidential samples is treated as "confidential." Upon receipt of confidential information, the DCO* logs these documents into a Confidential Inventory Log. The information is then made available to authorized personnel, but only after it has been signed out to that person by the DCO. The documents shall be returned to the locked file at the conclusion of each working day. Confidential information may not be reproduced except upon approval by and under the supervision of the DCO. Any reproduction must be kept to an absolute minimum. The DCO will enter all copies into the document control system and apply the same requirements as the original. In addition, this information may not be destroyed except upon approval by and under the supervision of the EPA program manager and EPA contracting officer. The DCO shall remove and retain the cover page of any confidential information disposed of for one year and shall keep a record of the destruction in the Confidential Inventory Log.

*DCO is a document control officer assigned by the contractor to maintain control of confidential information.

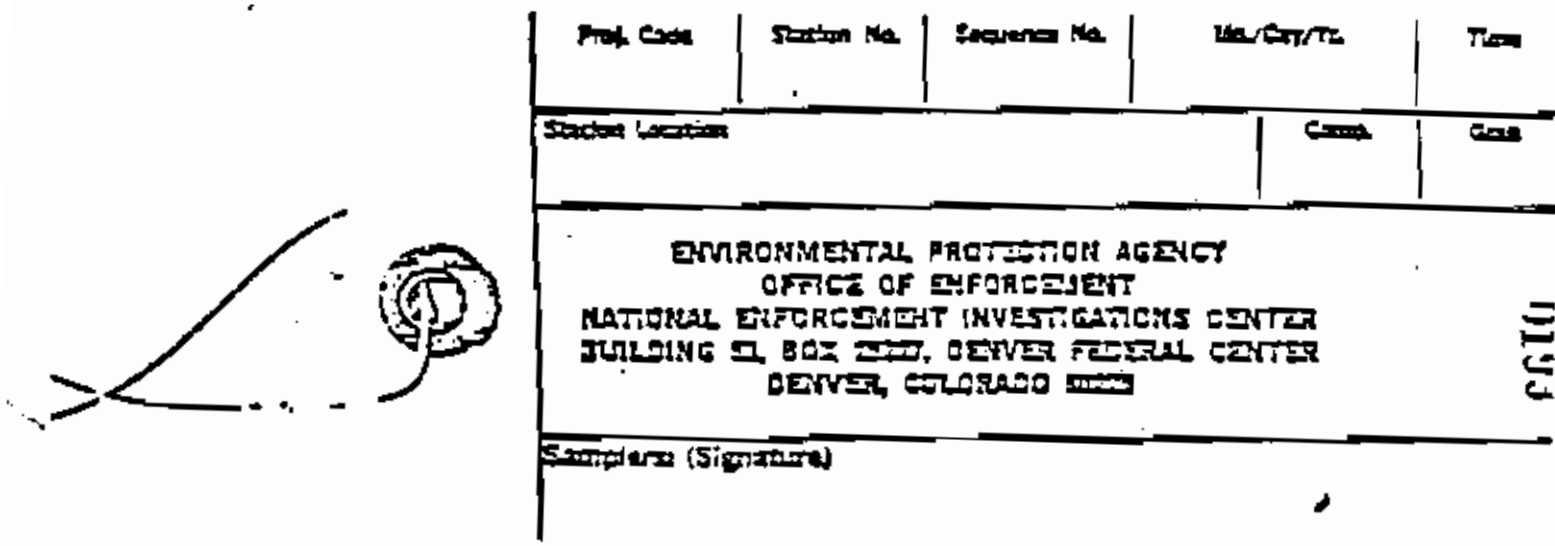


Figure 1. Example sample tag.

Figure 3. Example custody seal made of perforated paper stock.

PROJ. NO | PROJECT NAME

Figure 2. n-of-Custody Record

MPLERS: (Signature)

A. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS							REMARKS

linquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Inquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Inquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment; Copy to Coordinator Field *

Exhibit C
Page 7 of 8

1. Study plans or project plans.
2. Sample traffic records, weekly reports.
3. Custody records, sample tags, sample loop.
4. Laboratory logbooks, personal logbooks, instrument logbooks.
5. Laboratory data (sortad by sample), calibration and quality control results.
6. Data summaries and reports.
7. All other documents, forms or records referencing the samples.

Figure 4. Example Document Inventory Format for Each Case.

IFB WA 85-J176
WA 85-J177
WA 85-J178

ATTACHMENT A

USEPA Contract Laboratory Program

STATEMENT OF WORK

for

ORGANICS ANALYSIS

Multi-Media

Multi-Concentration

5/84

Revised: 1/55

CLP ORGANICS ANALYSIS SOW: INDEX TO 1/85 REVISION PAGES

Page	Location of Revision
A-7	Section 7.
B-4	Section (C.) 12. & 13.; Section D. 1, 2 and 3; and Section E. C-9) and D-1).
B-4a	Sections F and F.1.
B-19, B-19a & B-20	Section III.
B-20 & B-20a	Section IV. E, F, G and H.
B-21	Section V. A, B, C.2, C.3.e. and D.2.
B-22	Section (D.) 3.b.1; and Sections E.2 and E.3.b.1.
B-24	Section (4).
B-28	Form I, top left - SMO address removed.
B-29, B-30 & B-31	Form I, top left - SMO address removed; Lab Name and Case No. lines added.
B-36	Section C: paragraphs 3, 4, and 5.
B-37 & B-38	Form III, Column 3, "Conc. Spike Added" - unit (ug/L).
B-44	Section F - Standard Deviation formula; "SD" abbreviation; and asterisked footnote.
B-47	Form VI (page 2) - flag for benzidine in RF_{50} column and associated footnote.
B-50 & B-51	Form VII - flags in componnd column and associated footnote.
B-52	Section H. paragraph 3, Equation 1.1, paragraph 4, and "Nota" at bottom of page.
B-53	Paragraphs 1 and 2, Equation 1.4, Equation 1.5, RT_s definition, and "Note" at bottom of page.
B-54	Form VIII: Linearity section - footnote (1); Breakdown section - "COMBINED $^{(2)}$" column and associated footnote.
B-55	Paragraph 5 (following Eq. 1.6); and "Note" at bottom of page.
B-56	Form IX, asterisked footnote.
C-4	Item 90. Benzidine - detection limits.
C-6	Low Soil/Sediment Detection Limits; footnute "f".
D-9	Sections 1.4.4. and 1.4.4.1.
D-9a	Page Shift.
D-18	Sections 2.4.7.2 and 2.4.8.
D-28	Section 1.5.11.
D-29	Section 1.7.1.1.

1/85 Organic SOW Revisions (cont. - 2)

Page	Location of Revision
D-30	Section 1.7.1.9.
D-31	Section 1.7.2.2.1 renumbered to 1.7.2.1.1.
D-39	Lines 1 and 3.
D-40	Line 2; and Section 2.5.1.
D-41	Sections 2.5.2.2. and 2.5.2.3.
D-44a	Section 2.7, last sentence; and Section 2.7.1, line 1.
D-45	Section 2.7.2, lines 1, 13 and 14.
D-55	Section 1.5.1.
D-65	Section 1.2.2, last 2 sentences.
D-99	Section 2.4.4.1, line 8.
D-104	Last line of page (deleted).
D-109	Table 5 - secondary ions for arachlors 1221 and 1232; and Table 6 - secondary ions for 1,4-dichlorobenzene-d_4.
D-110	Section 3.3.1, second sentence.
D-113	Section 3.5.2.1, last sentence.
D-113a	Sections 3.6 and 3.6.1.
D-114 & D-114a	Section 3.6.1.1, lines 6-8; and Section 3.6.1.2.
D-115	Line 5.
D-116	Section 3.6.2.2.3.
D-118, D-118a D-118b, D-119 & D-119a	Section 3.6.3.4; and Sections 3.7.1 through 3.7.3.4.
D-121	Section 3.8.1.
D-122	Lines 2,4,5 and 11; and Section 3.8.8, last sentence.
D-123	Section 3.9.1.5, first word of line 2.
D-124	Table 7 - asterisk following title (and asterisk after column 1 heading deleted).
E-8	Section 1.1, last 2 sentences.
E-16	Section 1.3, line 4 and last 2 sentences.
E-17	Table definition (last paragraph).
E-22	Sections 2.1.1 and 2.1.2.
E-23	Section 2.3.1.
E-24	Section 2.4.1, bromoform definition following table.

1/85 Organic SOW Revisions (cont. - 3)

Page	Location of Revision
E-26	Section 2.6.1, last sentence.
E-27	Section 2.6.3.2.
E-28	Sections 3.0, 3.1.1, 3.1.2. and 3.2.1.1.
E-28a	Page shift.
E-29	Table 4.1 - asterisks in heading and asterisked footnote.
E-37	Section 7.2.2.3.
E-38 thru E-41d	All.
E-54 thru E-70	All.

STATEMENT OF WORK

TABLE OF CONTENTS

EXHIBIT A

Summary of Requirements

GENERAL REQUIREMENTS

The Contractor shall use proven instruments and techniques to identify and measure the concentrations of volatile, semi-volatile and pesticide Hazardous Substance List (HSL) compounds listed in Exhibit C. The Contractor shall prepare extracts and dilutions of hazardous waste samples. The Contractor shall, optionally, screen extracts (soil characterization mandatory) at an initial extract concentration. Then, based on the screening response, use specific analytical methods described in Exhibit D to extract and concentrate sample extracts to achieve the Contract Required Detection Limits (CRDL) listed in Exhibit C. Exhibit D lists the analytical methods and starting points to be achieved for each of the HSL target compounds. Additionally, the Contractor shall conduct a survey to determine the possible identity of up to ten (10) unknown volatile components and up to twenty (20) unknown semi-volatile components (in addition to those listed in Exhibit C) in each sample analyzed by GC/MS. The Contractor shall employ state-of-the-art GC/MS and/or GC procedures to perform all analyses of samples submitted, including all necessary preparations for analysis.

The samples to be analyzed by the Contractor are from known or suspected hazardous waste sites and samples may contain potentially hazardous organic and/or inorganic materials at potentially high concentration levels. The Contractor should be aware of the potential hazards associated with the handling and analyses of these samples. It is the Contractor's responsibility to take all necessary safety measures to ensure his employees safety.

SPECIFIC REQUIREMENTS

The Contractor shall use his analytical experience and equipment to perform qualitative and quantitative analyses of the organic chemical pollutants listed in Exhibit C. Preparation of the samples shall be done as described in Exhibit D. The Contractor shall follow the protocols established by the USEPA for sample preparation, analysis, storage and preservation before and after the analysis (see Exhibit D).

During preparation, the Contractor shall fortify all samples, blanks, matrix spikes, and matrix spike duplicates with surrogate spiking compounds (listed in Exhibit E). Additionally, all sample semi-volatile extracts and aliquots for volatile organics analysis shall be spiked with internal standard compounds (listed in Exhibit E) before injection or purging.

In Exhibit D, the EPA provides the Contractor with the specific analytical procedures to be used along with the definition of the specific application of these methods to this contract. This includes instructions for sample preparation, gas chromatographic screening, mass spectrometric identification

and data evaluation. Specific ions used for searching the mass spectral data for each compound are included.

1. For each sample, the Contractor shall perform the following tasks:

Task I. Receive and Prepare Hazardous Waste Disposal Site Samples.

a. Receive and handle samples under the chain-of-custody procedures described in Exhibit F.

b. Prepare samples as described in Exhibit D. VOA analyses shall be performed within 7 days of VTSR for water samples and within 10 days of VTSR for soil samples. Sample extractions shall be completed within 5 days of VTSR for water samples and within 10 days of VTSR for soil samples. Sample extracts must be completely analyzed within 40 days of extraction. (Note: This does not preclude the contract requirement of a 30-day turnaround of analytical data.)

Task II. Extraction and Analysis for Identity of Specific Organic Compounds.

a. Extracts and diluted aliquots prepared in Task I shall be analyzed by GC and GC/MS techniques given in Exhibit D for the hazardous substances referenced in Exhibit C.

b. The target compounds listed in Hazardous Substances List (HSL), Exhibit C, shall be identified as described in the methodologies given in Exhibit D. Automated computer programs may be used to facilitate the identification.

Task III. Qualitative Verification of the Compounds Identified in Task II.

a. The compounds initially identified in Task II shall be verified by an analyst competent in the interpretation of mass spectra (see Bidder Pre-Award Laboratory Evaluation Criteria) 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. This procedure requires the use of multiple internal standards.

b. 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 calibration standard must be run on the same 12-hour time period as the sample.

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 and BFB daily tuning requirements of Tables 1.1 and 1.2 in Exhibit E. The standard spectra used may be from a laboratory generated library or obtained from the calibration standard run used to obtain reference

RRTs. These requirements for qualitative verification by comparison of mass spectra are as follows:

(1) All ions present in the standard mass spectrum at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.

(2) The relative intensities of ions specified in (1) must agree within plus or minus 20 percent between the standard and sample spectra.

(3) Ions greater than 10 percent 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.

Task IV. Quantification of Compounds Verified in Task III.

a. The Contractor shall quantify components identified in Task II and verified in Task III by the internal standard method stipulated in Exhibit D. Where multiple internal standards are required by EPA, the Contractor shall perform quantitation utilizing the internal standards specified in Exhibit E, part 2, Tables 2.1 or 2.2.

b. The Contractor shall determine response factors for each 12-hour time period and shall include a calibration check of the initial five point calibration as described in Exhibit E.

Task V. Tentative Identification of Non-HSL Sample Components.

a. For each sample, the Contractor shall execute a maximum of thirty (30) library searches on substances not listed in Exhibit C. The 10 substances of greatest apparent concentration not listed in Exhibit C for each volatile organic fraction, and the 20 substances 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 most recent available EPA/NIH mass spectral library. (Substances with responses less than 10 percent of the nearest internal standard are not required to be searched in this fashion). Only after visual comparison of sample spectra with the spectra from the library searches will the mass spectral interpretation specialist assign a tentative identification. If the unknown does not meet the identification criteria of Task III, it should be reported as unknown.

Task VI. Quality Assurance/Quality Control Procedures

a. All specific quality assurance procedures prescribed (Exhibit E, QA/QC Requirements) shall be strictly adhered to by the Contractor. Records documenting the use of the protocol shall be maintained in accordance with the document control procedures prescribed in Exhibit F, and reported in accordance with Exhibit B, "Reporting Requirements and Deliverables"

b. The Contractor shall perform one spiked sample analysis and one duplicate spiked sample analysis on each group of samples of a similar matrix and concentration level for each Case* of samples received or for each 20 samples, whichever is more frequent. The Contractor shall prepare and analyze one laboratory reagent blank for each group of samples of a similar matrix and concentration level for each Case of samples received or for each 20 samples, or whenever samples are extracted, whichever is more frequent. (Volatile analysis requires one instrument blank for each 12-hour time period when volatile HSL compounds are analyzed.) Samples, blanks, matrix spikes and matrix spike duplicates shall be carried through the entire analytical process from extraction to final GC/MS or GC-ECD analysis, including all data reporting requirements and magnetic tape data storage.

Additionally, the contractor shall perform instrument calibration (by "hardware tune") and performance audits for each twelve hour time period to include: Decafluorotriphenylphosphine (DFTPP) and/or bromofluorobenzene (BFB) as applicable and a specific calibration standard(s) for response, retention time and mass spectra. Additional quality control shall be conducted in the form of the analysis of Performance Evaluation check samples submitted to the laboratory by EPA. The results of comparison studies are due within thirty calender days of receipt of the samples. A scoring penalty will be assessed for PE data delivered to EPA 31 days or later, after the documented day of sample receipt. The results of all such control or PE check samples may be used as grounds for termination of noncompliant contractors. "Compliant performance" is defined as that which yields correct compound identification and concentration values as determined by EPA. (See Section IV, Exhibit E.)

c. After award of contract and before the first sample results are due, the contractor shall determine the analytical instrument detection limits. The contractor should compare these instrumental detection limits with sample detection limits to determine if in-house quality control procedures are effective. Using standard reference materials, the Contractor shall perform 3 analyses of standards for all components being measured at 3-5 times the required detection limit concentrations (see Exhibit C). These analyses shall be performed using the instrumental conditions in Exhibit D on standards in solvent for base/neutrals, acids, and pesticides/PCBs and on standards diluted into reagent water for volatile organics. The instrument detection limits shall be calculated as 3 times the standard deviation of the measured values. These values shall be supplied to the data users (see Exhibit B, "Reporting Requirements and Deliverables"). Pesticide and PCB detection limits shall be determined by both GC and GC/MS analysis respectively.

2. EPA will provide to the Contractor formats for the reporting of all data (see Exhibit B, "Reporting Requirements and Deliverables"). The Contractor shall be responsible for completing and returning laboratory and chemical analysis data sheets and weekly reports within the time specified in the contract schedule. Use of forms in formats other than those supplied by EPA will be deemed as non-compliance. Such data are unacceptable. Resubmission, at no

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* A Case consists of a finite, usually predetermined number of samples collected over a given time period from a particular site.

additional cost to the government, in the specified format will be required. Computer generated forms may be submitted provided the forms are in EXACT EPA FORMAT. This means that the order of data elements is the same as on each EPA required form.

3. The Contractor shall provide analytical equipment and technical expertise for this contract as specified below:

a. The Contractor shall have sufficient gas chromatograph (GC) and gas chromatograph/mass spectrometer/data system (GC/MS/DS) capability to meet all the terms and conditions of the Contract. The Contractor shall provide adequate instrument redundancy to ensure that at least one operating GC and GC/MS/DS may reasonably be expected to be available at any one time. This instrument redundancy may be demonstrated by either having more than one operational GC and GC/MS/DS inhouse or through extensive in-house stocks of replacement parts and circuit boards. The Contractor shall maintain, at the minimum, all analytical equipment allocated for this contract at the time of award.

b. The Contractor's instrument systems shall have the following:

(1) The GC/MS shall be equipped with a glass jet separator.

(2) The computer shall be interfaced by hardware to the mass spectrometer and be capable of acquiring continuous mass scans for the duration of the chromatographic program.

(3) The computer shall be equipped with mass storage devices for saving all data from the GC/MS runs.

(4) Computer software shall be available to allow searching GC/MS runs for specific ions and plotting the intensity of the ions with respect to time or scan number.

(5) The GC/MS shall be equipped with a split/splitless injector and GC to MS interface capable of extending a fused silica capillary column into the ion source. The column is to be 30 meters long by 0.25 or 0.32 mm inside diameter, bonded DB-5, fused silica or equivalent.

(6) The GC for pesticide analysis shall be performed using packed columns (see Exhibit D, Section IV, for an optional FSCC conformation column) and shall be equipped with a detector suitable for pesticide analysis as described in Exhibit D.

c. The Contractor shall use a magnetic tape storage device capable of recording data suitable for long-term off-line storage. The Contractor shall retain all raw GC/MS data acquired during the entire contract period on magnetic tape in appropriate instrument manufacturer format. The Contractor shall provide the magnetic tapes to the USEPA within 180 days after contract expiration or within seven (7) days of request by the Project Officer.

d. The Contractor shall have access to a computerized MS library search system capable of providing a forward comparison, utilizing the standard spectra contained in the EPA/NIH Mass Spectral Data Base. The most recent available EPA/NIH Mass Spectral Library should be used.

(1) The system shall provide a numerical ranking of the standard spectra most closely corresponding to the sample spectra examined.

(2) The data system shall remove background signals from suspect chemical pollutant spectra.

e. The Contractor shall use, in-house (at contractor's facility) and operable, a device capable of analyzing purgeable organics as described in Exhibit D.

4. The Contractor shall designate and utilize key personnel meeting the minimum requirements, as set forth in items a through e below, to meet all the terms and conditions of the contract. The EPA reserves the right to review personnel qualifications and reject those not meeting the minimum required experience.

a. The Contractor's GC/MS operators performing work on this contract shall each have at least 9 months experience in the operation of the GC/MS/DS on environmental samples.

b. The Contractor's mass spectral interpretation specialist performing work on this contract shall have at least 2 years of experience (as used herein, "experience" is deemed to mean, "more than 50 percent of the personnel's productive work time") in the interpretation of mass spectra gathered in GC/MS analysis.

c. The Contractor's extraction and concentration specialist performing work on this contract shall have at least 1 year experience in the preparation of extracts from environmental or hazardous waste samples.

d. The Contractor's purge and trap specialist performing work on this contract shall have at least 6 months experience using the purge and trap technique for volatile organics.

e. The Contractor's pesticide residue analysis specialist performing work on this contract shall have at least 2 years experience in organochlorine pesticide residue and PCB analysis, including clean-up procedures such as column chromatography, on environmental samples.

5. The Contractor shall preserve all sample extracts after analysis in bottles/vials with Teflon-lined septa and maintained at 4°C. Within 180 days after data submission, the Contractor shall request the Project Officer for authorization to dispose of sample extracts or provide the sample extracts to the USEPA within seven (7) days after a request by the Project Officer or the Sample Management Office (SMO).

6. The Contractor shall adhere to chain-of-custody procedures described in Exhibit F. Documentation, as described therein, shall be required to show that all procedures are being strictly followed. This documentation shall be reported as the complete Case file purge (see Exhibit B).

7. Sample shipments to the Contractor's facility will be scheduled and coordinated by the EPA CLP Sample Management Office (SMO).

a. The Contractor shall communicate with SMO personnel by telephone as necessary throughout the process of sample scheduling, shipment, analysis and data reporting, to ensure that samples are properly processed. This shall include immediately notifying SMO personnel of any irregularities with samples or sample paperwork received (noting discrepancies from verbal order placed by SMO), problems encountered in sample analyses that will affect the data produced, and laboratory conditions that impact on timeliness of analyses and data reporting. In particular, the Contractor shall notify SMO personnel in advance regarding sample data that will be late and shall specify an estimated delivery date.

b. Sample analyses will be scheduled by groups of samples, each defined as a Case and identified by a unique SMO Case number. A Case signifies a group of samples collected at one site or geographical area over a predetermined time period, and will include one or more field samples with associated blanks. Samples may be shipped to the Contractor in a single shipment or multiple shipments over a period of time, depending on the size of the Case.

c. Each sample received by the Contractor should be labeled with a SMO sample number, and accompanied by a Traffic Report form bearing the sample number and descriptive information regarding the sample. The Contractor shall complete and sign the Traffic Report, recording the date of sample receipt and sample condition on receipt for each sample container. The Contractor shall submit the signed copy of each Traffic Report to SMO within seven (7) calendar days following sample receipt (see contract delivery schedule). If there are problems either with the samples (e.g., mixed media, containers broken or leaking) or paperwork (e.g., Traffic Reports not with shipment, sample and Traffic Report numbers do not correspond) the Contractor shall immediately contact SMO for resolution.

d. The SMO Case and sample numbers shall be used by the Contractor in identifying samples received under this contract both verbally and in reports/correspondence.

e. Samples will routinely be shipped to the Contractor through an overnight delivery service. However, as necessary, the Contractor shall be responsible for any handling or processing required for the receipt of sample shipments, including pick-up of samples at the nearest servicing airport, bus station or other carrier service within the Contractor's geographical area. The Contractor shall be available to receive sample shipments at any time the delivery service is operating, including Saturdays.

f. The Contractor shall accept all samples scheduled by SMO, provided that the total number of samples received in any calendar month does not exceed the monthly limitation expressed in the contract. Should the Contractor elect to accept additional samples, the Contractor shall remain bound by all contract requirements for analysis of those samples accepted.

EXHIBIT B

Reporting and Deliverables Requirements

EXHIBIT B

TABLE OF CONTENTS

REPORTING AND DELIVERABLES REQUIREMENTS

The Contractor laboratory shall provide reports and other deliverables as specified in the Contract Schedule. These reports are described in Section I of this Exhibit. All reports must be submitted in a legible form or resubmission will be required at no additional cost to the Agency. All reports and documentation required, including chromatograms, reconstructed ion chromatograms and mass spectra, must be clearly labeled with the Sample Management Office Case number and associated Sample/Traffic Report number(s). Reports and documentation must be submitted arranged clearly in the order specified in Section II, Deliverables Index, located within this Exhibit. Section III contains all the required Forms, in the Agency specified formats, along with complete instructions to assist the Contractor in accurately providing the Agency all required data. If the documentation is submitted without the required identification or not in the required order, resubmission will be required at no additional cost to the Agency.

SECTION 1 - REPORT DESCRIPTION

The summary which follows describes the specific reports required to meet all reporting requirements of this Contract.

A. Weekly Progress Report - Weekly report (Figure 1-1) specifying number of samples received in week and deliverables, recorded by Case number, sample number, type of deliverable, expected date of submission, and reason for lateness.

B. Sample Traffic Report - Copy of SMO Sample Traffic Report with Lab receipt information and signed in original Contractor signature.

C. Sample Data Package - Data report for analyses of each sample to include:

Sample Traffic Reports: Copies of completed SMO Sample Traffic Reports for all samples reported in data package.

Case Narrative: (Laboratory cover letter)

1. Contains the Case number, Sample Management Office Sample numbers, Contract number and detailed documentation of any Quality Control, sample, shipment and/or analytical problems encountered in a specific Case. Also included should be documentation of any internal decision tree process used along with a summary of corrective actions taken. The Case narrative must be signed in original signature by the Laboratory Manager or his designare.

GC/MS Analysis Data:

2. Tabulated results (identification and quantity) of the specified hazardous substances (Exhibit C), validated and signed in original signature by the Laboratory Manager or his designate (Form I).* Report results to two significant figures. For rounding rules, follow the EPA Handbook of Analytical Quality Control in Water and Wastewater Laboratories (EPA-600/4-79-019). On Form I, the appropriate concentration units should be circled. For example, ug/L for water samples or ug/Kg for soil/sediment samples. No other units are acceptable.

3. Tabulated list of the highest probable match for each of the major compounds not listed in Exhibit C (up to 10 compounds per volatile fraction and up to 20 compounds per semi-volatile fraction), including the CAS (Chemical Abstracts Registry) number, tentative identification and estimated concentrations. For estimating concentration, assume a response factor of 1, and estimate the concentration by comparison of the compound peak height to the peak height of the nearest internal standard free of interferences on the reconstructed ion chromatogram.

4. a) Reconstructed total ion chromatograms for each sample extract, normalized to the largest non-solvent component (Example 1.1). Internal standard and surrogate spiking compounds are to be labeled and identified with their chemical names. If automated data system procedures are used for preliminary identification and/or quantification of the Hazardous Substance List (HSL) compounds, the complete data system report must be included in all sample data packages in addition to the reconstructed ion chromatogram (Example 1.3). For laboratories which do not use the automated data system procedures, a laboratory "raw data sheet", which contains the following information, must be included in the sample data package in addition to the chromatogram.

- SMO sample number
- date and time of analysis
- RT or scan number of identified HSL compounds
- ion used for quantitation with measured area
- copy of area table from data system (Example 1.4)
- GC/MS instrument ID

b) Reconstructed total ion chromatograms for all tentatively identified compounds not listed in Exhibit C. Report all peaks and label those that cannot be identified as "unknown" after applying criteria requirements in Exhibit D, Section IV.

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* In the event that the Laboratory Manager cannot validate all data reported for each sample, he/she will provide a detailed description of the problems associated with the sample in the Case Narrative.

5. a) Copies of raw spectra and copies of background subtracted mass spectra of hazardous substance listed in Exhibit C (HSL) identified in the sample extract displayed together on a single page (Dual Display) with the corresponding background subtracted HSL standard mass spectra, or for data systems incapable of dual display provide:

b) Both raw and background subtracted mass spectra of hazardous substances listed in Exhibit C (HSL) identified in the sample extract (Example 1.5), along with the background subtracted HSL standard mass spectra, each on a single page.

c) Copies of mass spectra of hazardous substances not listed in Exhibit C and non-surrogates identified in C.3 above (Tentatively Identified Compounds) with associated best-match spectra (three best fit). (Example 1.6)

6. Copies of pesticide chromatograms. All chromatograms must be labeled with the following information:

- sample I.D. (SMO sample number from Traffic Report)
- volume injected (ul)
- date and time of injection
- GC column identification
- GC instrument identification
- positive identification must be labeled with the names of compounds, either directly out from the peak or on a printout of retention times if retention times are printed over the peak.

7. Copies of pesticide chromatograms from second GC column confirmation. Chromatograms to be labeled as in C.6 above.

8. GC/MS pesticide confirmation data to include the reconstructed ion chromatogram of sample(s) as described in C.4 preceding. For multi response pesticides/PCBs mass spectra of three peaks is sufficient for identification.

9. Results of surrogate spike analysis (Form II), to include all samples, blanks, matrix spike, and matrix spike duplicates.

10. Results of matrix spike duplicate analysis (Form III) and results of all required reagent blank analyses (Form IV).

11. Tuning and Mass Calibration Standard (Form V) for DFTPP and/or BFB for each twelve (12) hour time period. Form V must include summary of all samples, blanks, matrix spikes, matrix spike duplicates and standards analyzed under a specific tune.

12. Initial calibration data (initial 5 point calibration) for volatile and semi-volatile HSL compounds (Form VI) for each GC/MS system used to analyze samples. All Initial Calibration Data (Form VI) pertinent to each Case must be submittd.

13. Continuing calibration data for volatile and semi-volatile HSL compounds for each twelve (12) hour time period (Form VII) for each GC/MS system used to analyze samples.

14. Tabulation of current calculated instrument detection limits as determined by the Laboratory. This can be a completed Form I annotated "Laboratory Instrument Detection Limits."

15. Gel permeation chromatograms (if required).

D. Raw QC Data Package - to include:

1. Blanks: Signed tabulated results (Form 1), Tentatively identified compounds (Form 1, Part B), mass spectra and reconstructed ion chromatograms for each blank extract as in C.2 through C.5 preceding. Copies of chromatograms of pesticide blanks properly labeled as in C.6 preceding.

2. Matrix Spikes: Signed tabulated results (Form 1) of non-spiked HSL compounds detected, Tentatively identified compounds (Form I, Part B), reconstructed ion chromatograms and computer quantitation reports or legible facsimile for each matrix spike sample as in C.4 preceding. Spectra are not required.

3. Matrix Spike Duplicate: Signed tabulated results (Form I) of non-spiked HSL compounds detected, Tentatively identified compounds (Form 1, Part B), reconstructed ion chromatograms and computer quantitation reports or legible facsimile, for each matrix spike duplicate sample as in C.4 preceding. Spectra are not required.

E. Sample Data Summary Package - To include the following data from Sample Date Package (C) and Raw QC Data Package (D).

C-1) Case Narrative

C-2) Signed tabulated hazardous substances results (Form I)

C-3) Tentatively identified compounds (Form I, Part B)

C-9) Surrogate spike analysis results (Form II) by matrix: water and/or soil; for soil, by concentration (low or medium)

C-10) Matrix spike/matrix spike duplicate results (Form III) and reagent blank analysis results (Form IV)

D-1) Blanks - signed tabulated results (Form 1) and Tentatively identified compounds (Form 1, Part B).

12. Initial calibration data (initial 5 point calibration) for volatile and semi-volatile HSL compounds (Form VI) for each GC/MS system used to analyze samples. All Initial Calibration Data (Form VI) pertinent to each Case must be submitted.

13. Continuing calibration data for volatile and semi-volatile HSL compounds for each twelve (12) hour time period (Form VII) for each GC/MS system used to analyse samples.

14. Tabulation of current calculated instrument detection limits as determined by the Laboratory. This can be a completed Form I annotated "Laboratory Instrument Detection Limits."

15. Gel permeation chromatograms (if required).

D. Raw QC Data Package - to include:

1. Blanks: Signed tabulated results (Form I), Tentatively identified compounds (Form I, Part B), mass spectra and reconstructed ion chromatograms for each blank extract as in C.2 through C.5 preceding. Copies of chromatograms of pesticide blanks properly labeled as in C.6 preceding.

2. Matrix Spikes: Signed tabulated results (Form I) of non-spiked HSL compounds detected, reconstructed ion chromatograms and computer quantitation reports or legible facsimile for each matrix spike sample as in C.4 preceding. Spectra are not required.

3. Matrix Spike Duplicate: Signed tabulated results (Form I) of non-spiked HSL compounds detected, reconstructed ion chromatograms and computer quantitation reports or legible facsimile, for each matrix spike duplicate sample as in C.4 preceding. Spectra are not required.

E. Sample Data Summary Package - To include the following data from Sample Data Package (C) and Raw QC Data Package (D).

C-1) Case Narrative

C-2) Signed tabulated hazardous substances results (Form I)

C-3) Tentatively identified compounds (Form I, Part B)

C-9) Surrogate spike analysis results (Form II) by matrix: water and/or soil; for soil, by concentration (low or medium)

C-10) Matrix spike/matrix spike duplicate results (Form III) and reagent blank analysis results (Form IV)

D-1) Blanks - signed tabulated results (Form I) and Tentatively identified compounds (Form I, Part B).

F. Standards Data Package - In accordance with the contract delivery schedule, when submitting data for a sample or group or samples in a Case, the applicable standards data must be submitted. Standards data package to include:

1. Reconstructed ion chromatograms (RIC) and computer quantitation reports or legible facsimiles, as described in C.4 preceding, for each Initial and Continuing Calibration analysis and from any pesticide/PCB confirmation.

2. Pesticide standard chromatograms and data system printouts for all standards to include:

- Evaluation Standard Mix A
- Evaluation Standard Mix B
- Evaluation Staudard Mix C
- Individual Standard Mix A or B
- All multiresponse peaticides/PCBs
- All quantitation standards
- A copy of the computer reproduction covering the 100 fold range

All chromatograms are required to heve the following:

- Label all standard peaks for ell individual compounds either diractly out from the peak or on the printout of retention times if retention times ere printed over the peak.
- Label the chromatogram for multicomponent standards. (i.e.: Aroclor 1242, Toxaphene, Chlordane)
- List total ng injected for each atanderd.
- A printout of retention times and corresponding peek areas must eccompany each chrometogram.
- Date and time of injecrion
- GC column identification
- GC iostrument identification (see Example 1.2)

G. GC/MS Magnetic Tapes -

All raw GC/MS data (includiog samples, blanks, matrix spike, metrix spike duplicates, standards, DFTPP and BFB) must be stored on magnetic tape, in appropriate instrument manufacturers format. The Laboratory is required to maintain the GC/MS tapes at their facility for the entire contract period.

The Contractor shall retain the magnetic tapes until directed to ship them by the Project Officer or Sample Management Office. The Laboratory should retaic a written reference (Logbook) of tape files to EPA sample number, calibration data, standards, blanks, matrix spikes, and matrix spike duplicates. The reference should include samplr numbers, Case numbers, and identification of which QC data applies to which samples.

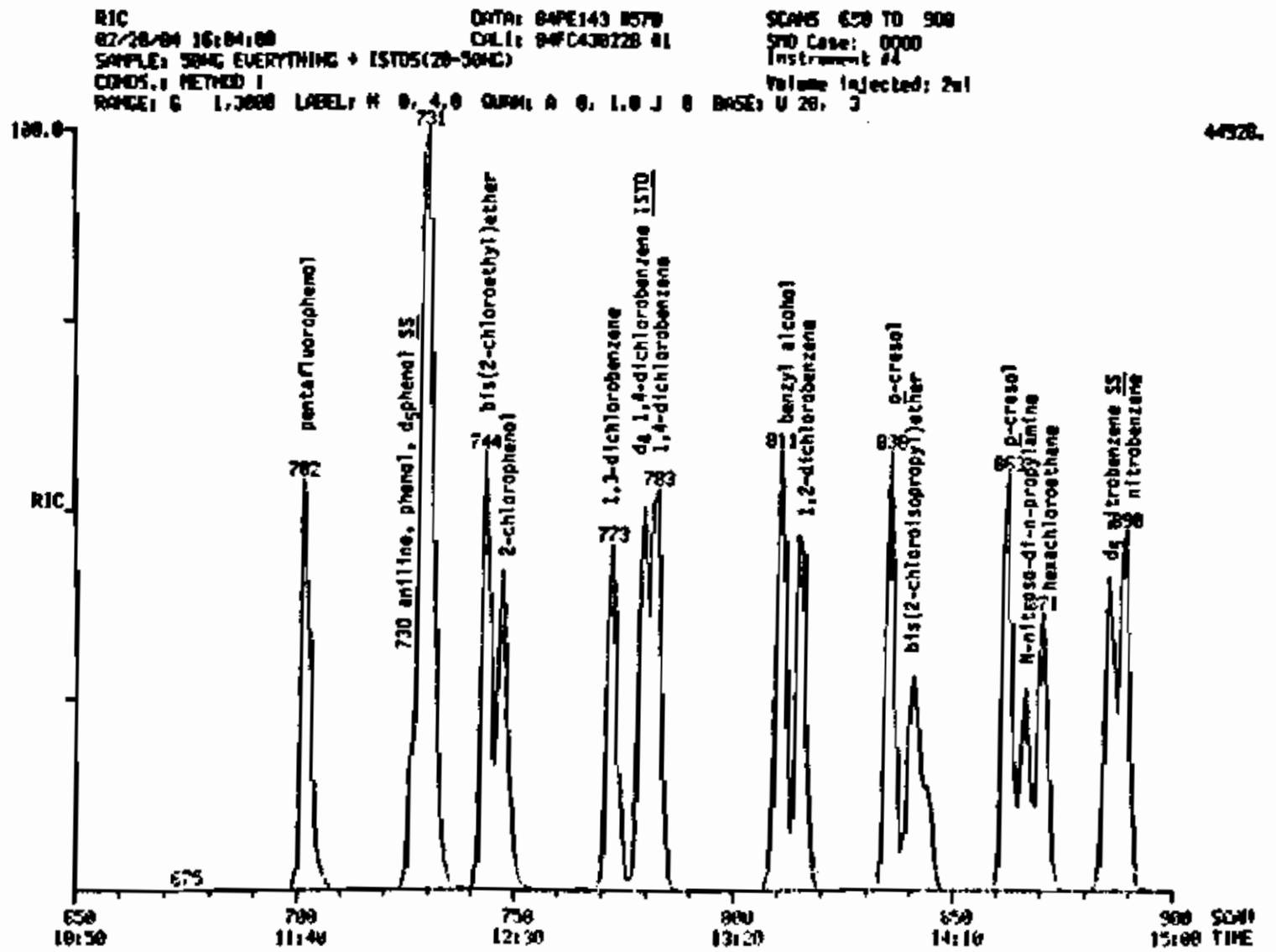
H. Extracts -

Sample extracts shall be preserved in bottles/vials with Teflon-lined septa and maintained at 4°C. Within 180 days after data submission, the Contractor shall request the Project Officer for authorization to dispose of sample extracts or provide the sample extracts to the USEPA within seven (7) days after a request by the Project Officer or the Sample Management Office (SMO).

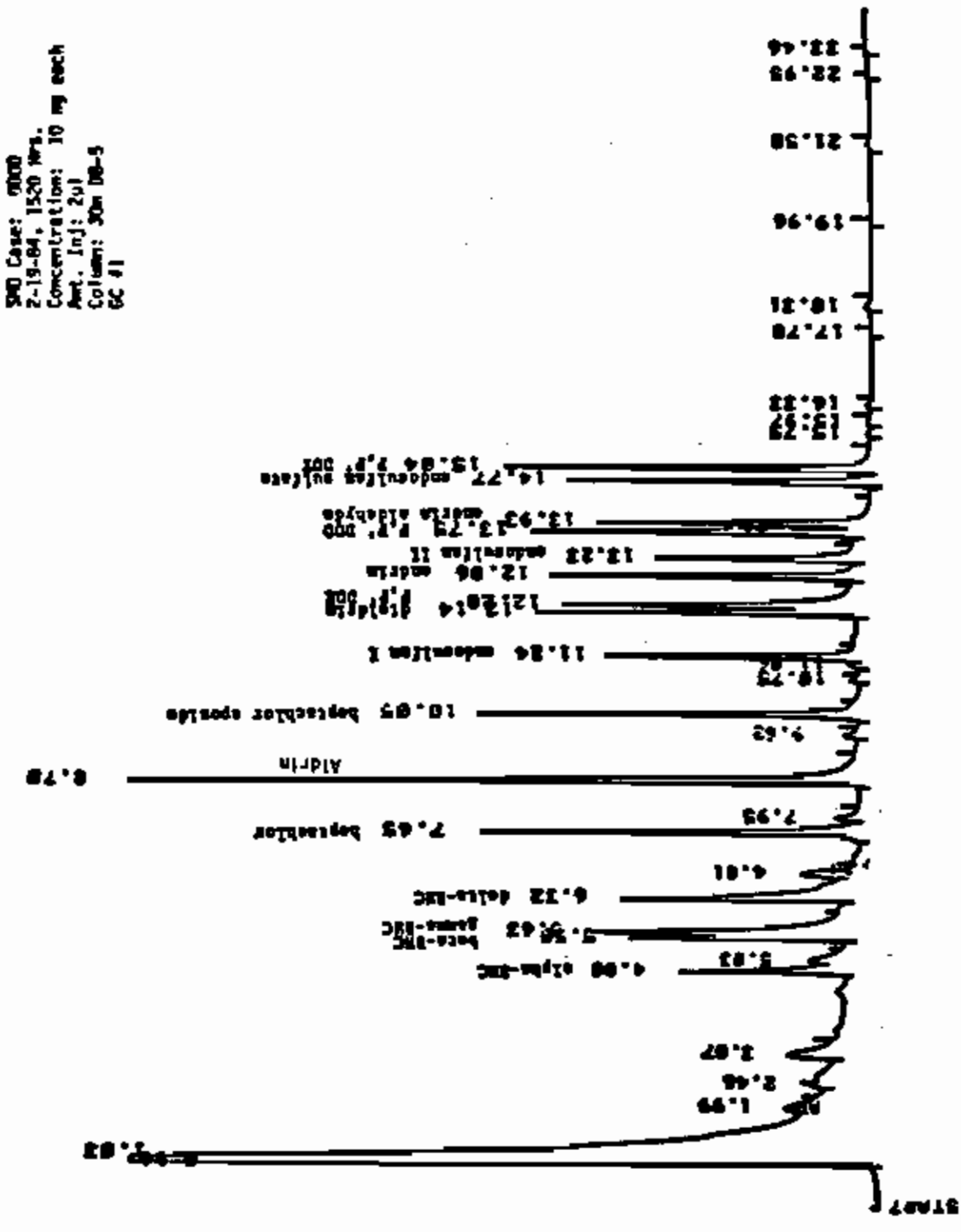
I. Complete Case File Purge - (formerly called the Document Control and Chain-of-Custody Package).

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, analysis logbook pages, bench sheets, chromatographic charts, computer printouts, raw data summaries, instrument logbook pages, correspondence, and the document inventory (see Exhibit F).

Note: Whenever the Laboratory is required to resubmit data as a result of an on-site laboratory evaluation or through a PO/DPO action, the data must be clearly marked as RESUBMITTED DATA and must be sent to all three contractual data recipients (SMO, EMSL-LV, and Region). A cover letter should be included which describes what data is being resubmitted, what SMO Case(s) it pertains to and who requested the resubmission.



Example 1.1. Reconstructed ion chromatogram.



Example 1.2. GC chromatogram of all single component pesticides on fused silica capillary column. See Exhibit D, Section IV, Table 1 for GC conditions.

```
QUANTITATION REPORT    FILE: 32VS010984

DATA: 32VS010984.T]
01/09/84 11:21:00
SAMPLE: 32VOASTD05,10SP1000,50-210XB,X10-701950,9UL/5ML          SMO Sample #0000
SUBMITTED BY:              ANALYST: FAM                          GC/MS # 1
                                                                 2-10-84, 1316 hrs

AMOUNT=AREA(HGHT) * REF.AMNT/(REF.AREA(HGHT)* RESP.FACT)
RESP. FAC. FROM LIBRARY ENTRY

 NO  NAME
  1  CHLOROMETHANE
  2  BROMOMETHANE
  3  VINYL CHLORIDE
  4  CHLOROETHANE
  5  METHYLENE CHLORIDE
  6  ETHENE,1,1-DICHLORO-
  7  METHANE,BROMOCHLORO-
  8  ETHANE,1,1-DICHLORO-
  9  1,2-TRANS-DICHLOROETHENE
 10  CHLOROFORM
 11  DA 1,2-DICHLOROETHANE
 12  ETHANE,1,2-DICHLORO-
 13  ETHANE,1,1,1-TRICHLORO-
 14  CARBONTETRACHLORIDE
 15  BROMODICHLOROMETHANE
 16  PROPANE,1,2-DICHLORO-
 17  1,3-TRANS-DICHLOROPROPENE
 18  TRICHLOROETHYLENE
 19  BENZENE
 20  CHLORODIBROMOMETHANE
 21  1,3-CIS-DICHLOROPROPENE
 22  ETHANE,1,1,2-TRICHLORO-
 23  2-CHLOROETHYL VINYL ETHER
 24  BENZENE, 1,4-DIFLUORO-
 25  BROMOFORM
 26  ETHENE,TETRACHLORO-
 27  ETHANE,1,1,2,2-TETRACHLORO-
 28  BB TOLUENE
 29  TOLUENE
 30  CHLOROBENZENE-D5
 31  CHLOROBENZENE
 32  ETHYLBENZENE
 33  P-BROMOFLUOROBENZENE
 34  M-XYLENE
 35  O & P-XYLENE (MIXED)

 NO  MAE  SCAN   TIME  REF   RRT  METH     AREA(HGHT)  AMOUNT       %TOT
  1   58    31   1:33   P  0.164  A EB       68188.   10.000 UG/L   1.77
  2   94    51   2:33   P  0.278  A EB      225085.   30.000 UG/L   1.07
  3   62    67   3:21   P  0.354  A EB       92049.   11.000 UG/L   1.16
  4   64    89   4:27   P  0.471  A EB       34561.   30.000 UG/L   1.07
  5   84   120   6:27   P  0.643  A EB      100410.   10.000 UG/L   1.03
  6   96   179   8:57   P  0.947  A EB       58221.   16.000 UG/L   1.65
  7  120   189   9:27   P  1.000  A BB       66096.   30.000 UG/L   2.29
  8   63   203  10:09   P  1.074  A BB      107720.   35.000 UG/L   1.65
  9   96   217  10:51   P  1.149  A EB       65227.   19.700 UG/L   1.94
```

Example 1.3. Automated quantitation report.

NO	PKI	RCMN	TIME	REF	RRT	METH	AREA(HEIGHT)	AMOUNT		RTOT
10	83	328	11:24	P	1.206	A BB	176375.	29.000	UG/L	8.46
11	65	346	12:00	P	1.278	A BB	184695.	102.297	R	10.87
12	87	342	12:06	P	1.289	A BB	81241.	21.900	UG/L	8.16
13	87	364	13:12	24	0.782	A BB	129320.	22.600	UG/L	8.22
14	117	371	13:33	24	0.721	A VB	144184.	26.100	UG/L	2.57
15	83	392	14:06	24	0.750	A BB	196909.	23.500	UG/L	2.31
16	63	306	15:18	24	0.814	A BB	87436.	20.300	UG/L	2.00
17	75	311	15:33	24	0.827	A BB	100339.	20.600	UG/L	2.03
18	130	321	16:03	24	0.854	A BV	88282.	20.500	UG/L	2.02
19	78	330	16:30	24	0.878	A BB	903545.	20.200	UG/L	1.99
20	129	333	16:39	24	0.886	A BV	154597.	27.800	UG/L	2.66
21	75	335	16:45	24	0.891	A BB	90621.	22.400	UG/L	2.21
22	97	335	16:45	24	0.891	A BB	69693.	22.300	UG/L	2.20
23	61	354	17:42	24	0.941	A BB	27784.	19.500	UG/L	1.95
24	114	376	18:48	24	1.000	A BB	297784.	31.400	UG/L	3.09
25	173	381	19:03	24	1.013	A BB	77846.	89.100	UG/L	2.57
26	164	424	21:12	30	0.918	A BB	77212.	21.700	UG/L	2.14
27	83	424	21:12	30	0.918	A BB	81795.	21.600	UG/L	2.13
28	89	444	22:12	24	1.101	A BV	262189.	103.853	R	10.22
29	91	447	22:21	30	0.959	A BB	239513.	20.500	UG/L	2.02
30	117	486	23:18	30	1.000	A BB	222545.	28.100	UG/L	2.26
31	112	488	23:24	30	1.004	A BB	166020.	19.900	UG/L	1.96
32	106	502	23:06	30	1.077	A BB	78468.	19.900	UG/L	1.86
33	95	546	27:18	30	1.172	A BB	945426.	95.978	R	9.55
34	106	577	28:51	30	1.238	A BB	87875.	29.100	UG/L	1.98
35	106	594	29:40	30	1.272	A BB	171778.	37.400	UG/L	3.68

Example 1.3. (continued).

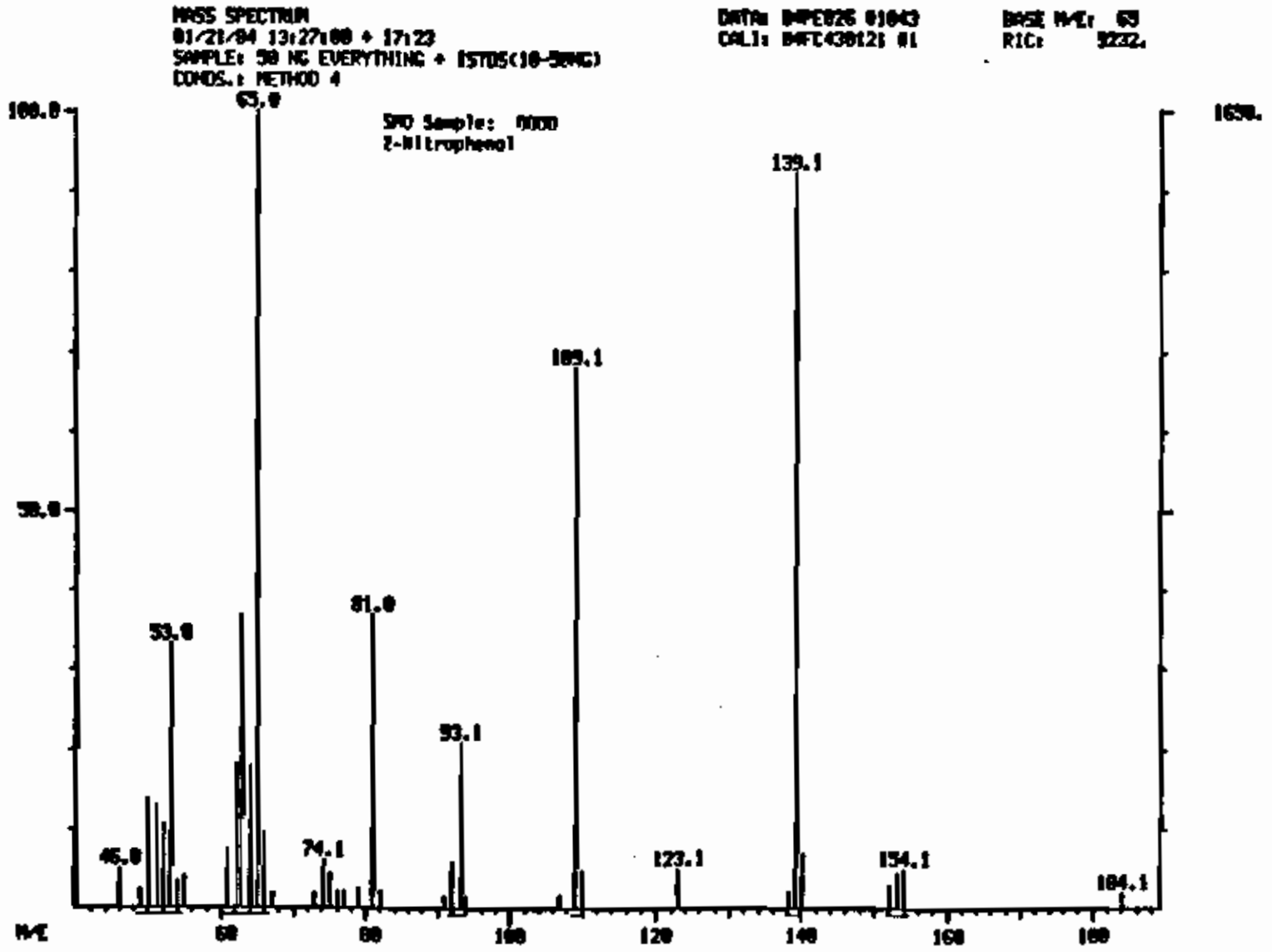
SMO Sample #1111 (BHA)
GC/MS # 2
2-19-84, 1016 hrs

FILE NUMBER 16000

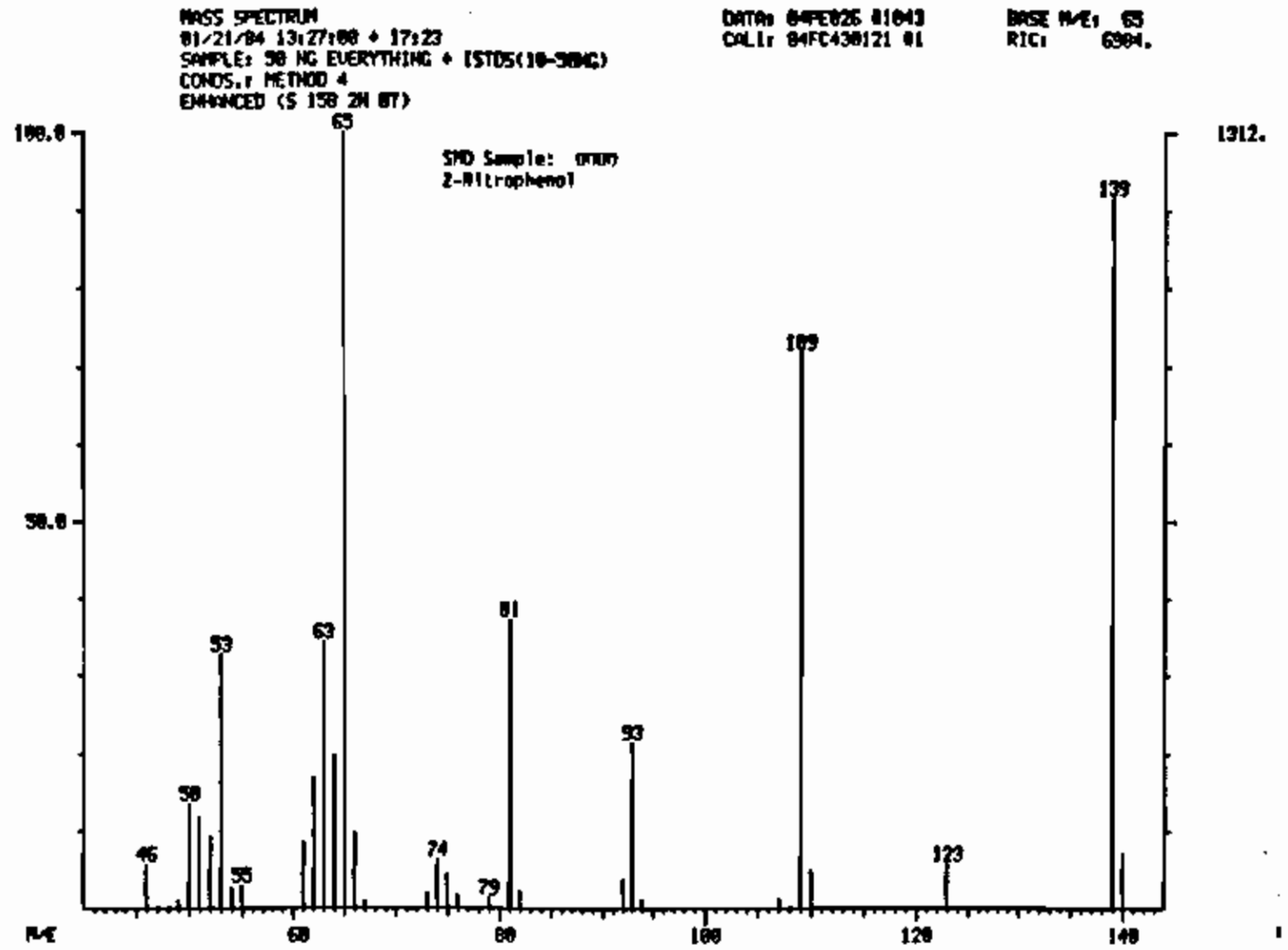
ENTRY	TIME	MASS	AREA	%
1	9.7	188.0	45848.	100.00
2	9.5	264.0	5316.	11.59
3	12.1	184.0	57578.	125.58

CAL % ON ENTRY?

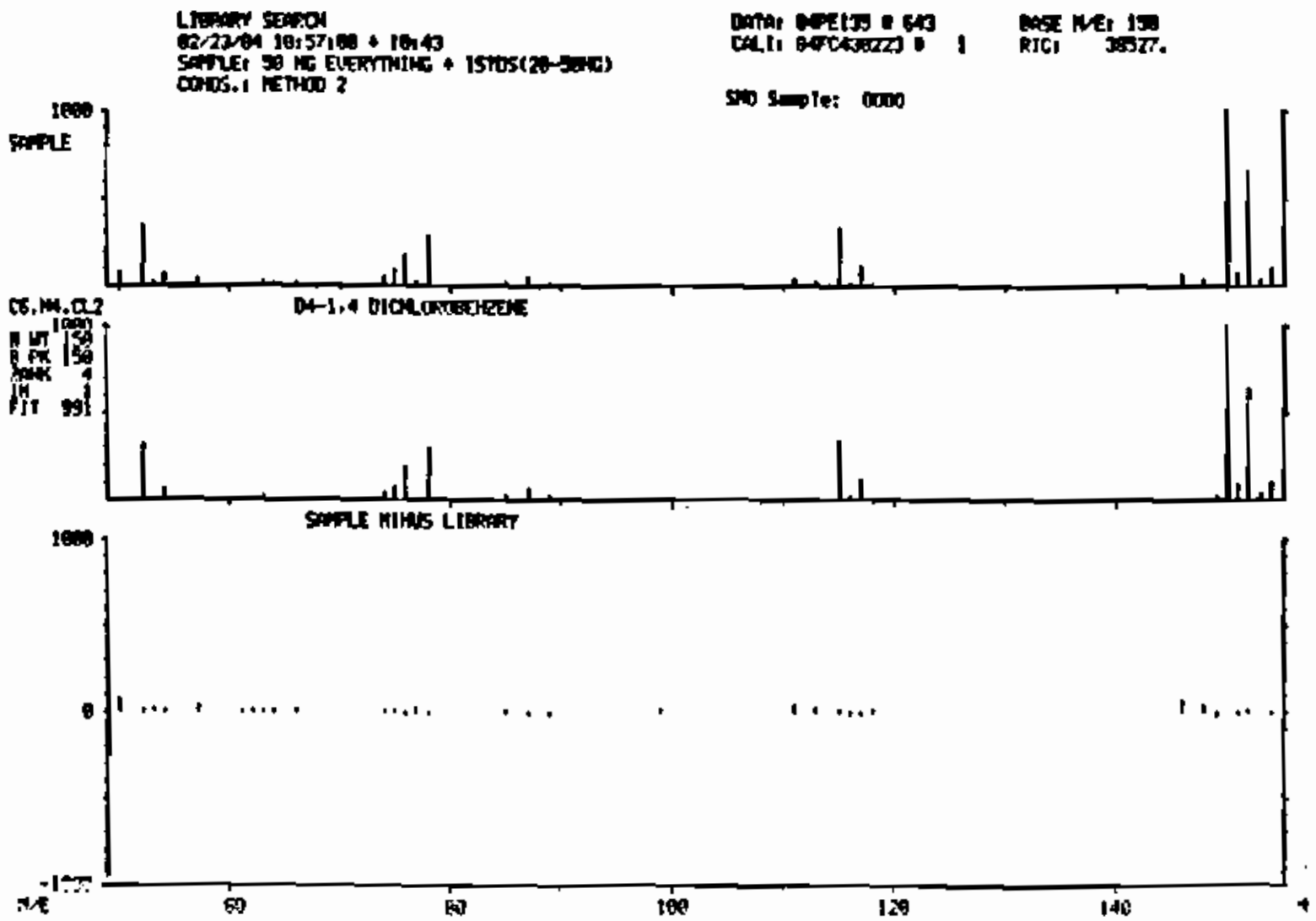
Example 1.4. Area table from data system.



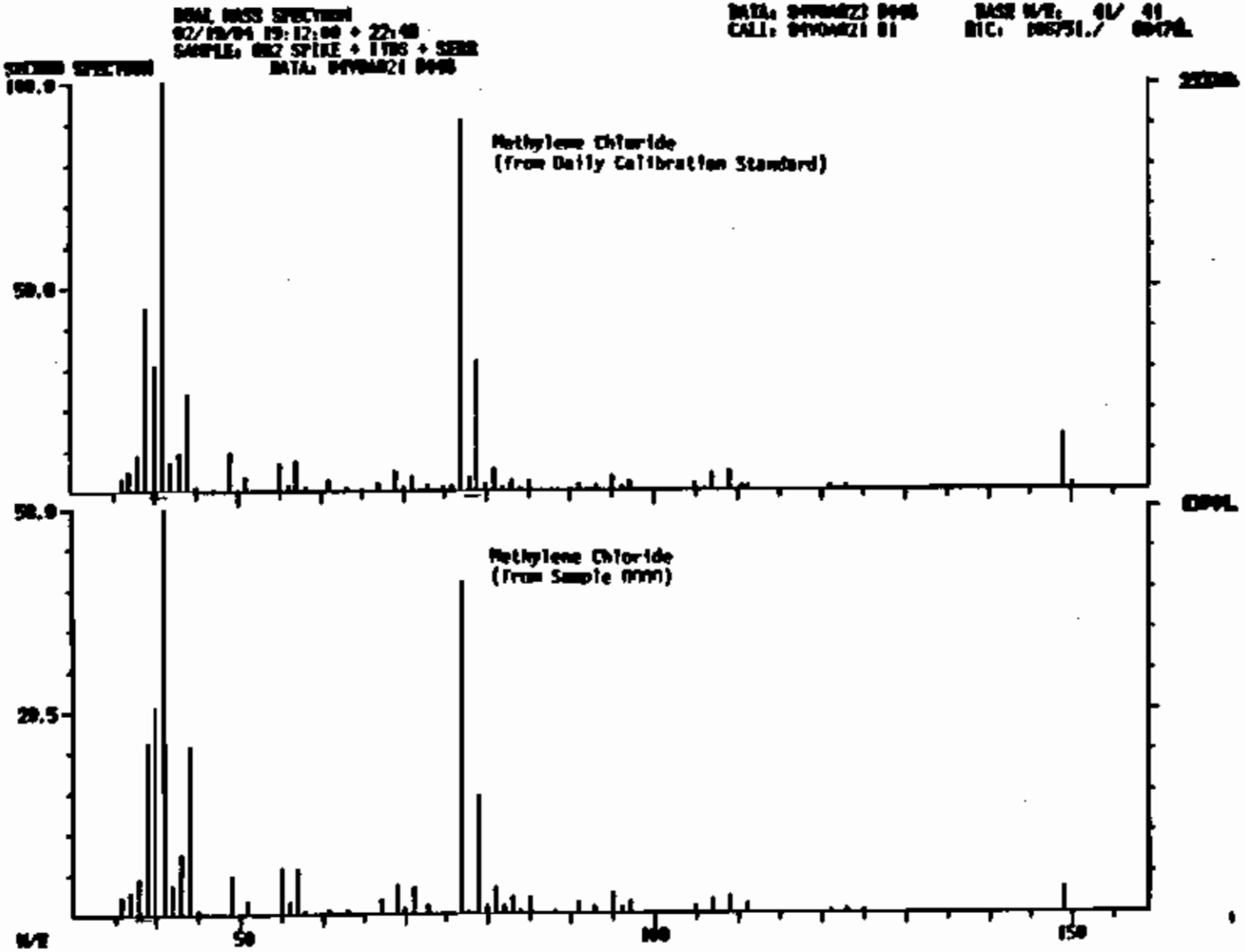
Example 1.5a. Raw HSL spectra.



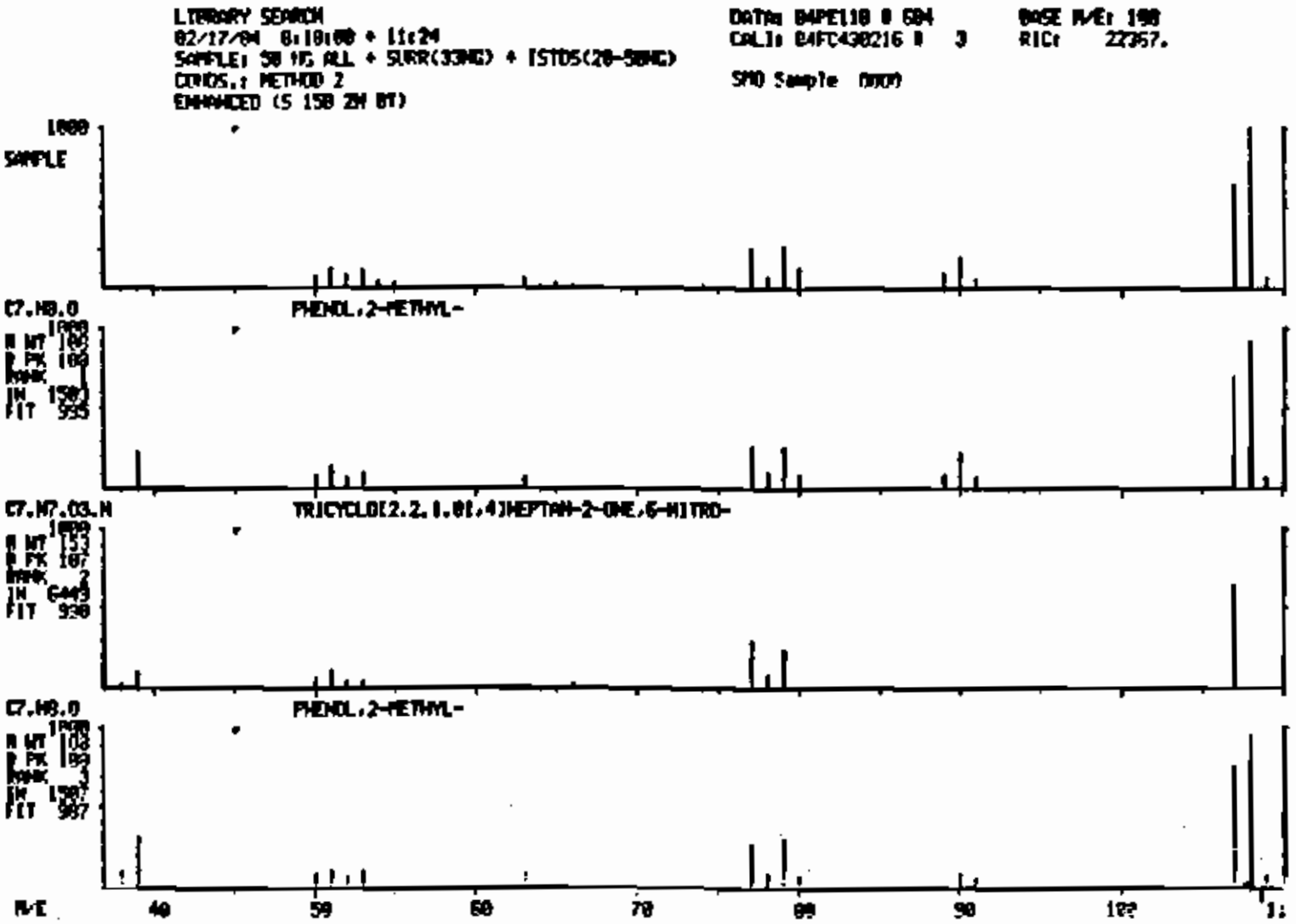
Example 1.5b. Background subtracted HSL spectra.



Example 1.5c. Dual display of sample spectra with laboratory generated standard library spectra.



Example 1.5d. Dual display of HSL sample spectra with HSL standard spectra from daily calibration standard.



Example 1.6. Best fit library search.

LABORATORY WEEKLY REPORT
Organics - GC/MS

Week of: _____ (Monday) to _____ (Saturday), 198__ Report No: _____

Laboratory Name: _____

Contract Number: 68-01-_____

No. of Samples Scheduled for Receipt this Week:	No. of Samples Received this Week:
_____	_____

Deliverable Status to Date*

No. of Volatile Analyses Late: _____

No. of Semi-Volatile (B/N/A) Extractions Late: _____

No. of Pesticide/PCB Extractions Late: _____

No. of Sample Data Reports Late: _____

*Complete Attachment A providing all requested information for each delinquent deliverable.

Figure 1.1.

Attachment A

DESCRIPTION OF DELINQUENT CONTRACT REQUIREMENTS

Case Number	Sample Number	Deliverable Type (check one)				Expected Date of Completion/ Submission	Reason for Lateness
		VOA	B/N/A Ext.	Pest/ PCB Ext.	Data		

5/84 Rev

SECTION II DELIVERABLES INDEX AND REPORTING SCHEDULE

This section provides the Contractor Laboratory with the specific order of deliverables. Arrange each section in the order specified, separate with rubber bands, paper clips or other means as needed. Refer to Figure 2.1, for the specific reporting schedule and Figure 2.2, for report distribution addressees.

The contract reporting schedule, including report distribution requirements, appears following the deliverables index, on pages B-23 and B-24.

DELIVERABLES INDEX

I. Case Narrative

The Case narrative must contain: Case number, Contract number, summary of any QC, sample, shipment and analytical problems, and documentation of all internal decision tree processes used. Outline problems encountered and final solutions. Be as specific and detailed as necessary.

II. QC Summary

A. Surrogate Percent Recovery Summary (Form II)

B. Matrix Spike/Matrix Spike Duplicate Summary (Form III)

C. Reagent Blank Summary (Form IV)
(If more than a single form is necessary, it must be arranged in chronological order.)

D. GC/MS Tuning and Calibration Standard (Form V)

1. DFTPP in chronological order; by instrument.
2. BFB in chronological order; by instrument.

III. Sample Data

A. Samples should be arranged in packets with the Traffic Report, the Organic Analysis Data Sheet (Form I), followed by the raw data for volatile, semi-volatile and pesticide sample fractions. These sample packets should then be placed in increasing SMO sample number order.

1. Copy of Sample Traffic Report

2. RSL Results - Organic Analysis Data Sheet (Form I)

3. Tentatively Identified Compounds (Form I, Part B) - Must be included even if no compounds are found; if so, indicate on form: "no volatile compounds found" and/or "no semi-volatile compounds found."

4. Raw data - in order: VOA, BNA, Pesticide

   a. Reconstructed ion chromatogram(s) (GC/MS), chromatogram(s)(GC)

   b. Data System Printout

   - Quantitation report or legible facsimile (GC/MS)
   - Integration report or data system printout (GC)
   - Calibration plots (area vs. concentration) for 4,4'-DDT, 4,4'-DDD, 4,4'-DDE or toxaphene (where appropriate)

c. Raw HSL mass spectra and the background subtracted HSL mass spectra with lab generated HSL standard spectra (Dual Display)

* data systems incapable of dual display shall provide spectra in order:

- raw HSL compound spectra

- enhanced or background subtracted spectra

- laboratory generated HSL standard spectra

d. GC/MS library search spectra for Tentatively Identified Compound(s) (TIC)

e. Quantitation/Calculation of tentative ID concentration(s)

f. Manual work sheets

g. GPC Chromatograms (if appropriate)

IV. Standards Data

A. Current list of laboratory calculated instrument detection limits for all HSL compounds.

B. Initial Calibration Data (Form VI) - in order: VOA, BNA; by instrument if more than one instrument used.

1. When more than one initial calibration is performed, the data must be put in chronological order. All initial calibration data must be included even for a specific Case.

C. Continuing Calibration (Form VII) - in order: VOA, BNA; by instrument if more than one instrument used.

1. When more than one Continuing Calibration is performed, forms must be in chronological order.

D. Pesticide forms in the following order:

1. Form VIII - Pesticide Evaluation Standards Summary (all GC columns)

2. Form IX - Pesticide/PCB Standards Summary (all GC columns)

3. Form X - Pesticide/PCB Identification (only required for positive results)

E. VOA standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for both the initial (five point) and all continuing (12 hour) calibrations. Spectra are not required.

F. BNA standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for the both initial (five point) and all continuing (12 hour) calibrations. Spectra are not required.

G. All pesticide Evaluation Standard(s) (A, B, and C) chromatograms and data system printouts in chronological order by GC column type.

H. All pesticide Individual Standard Mix (A or B) chromatograms and data system printouts in chronological order by GC column type.

I. Pesticide Quantitation standard(s) chromatograms and data system printouts.

V. Raw QC Data

A. DFTPP (For each 12-hour period, for each GC/MS system utilized)

1. Bar graph spectrum

2. Mass listing

B. BFB (For each 12-hour period, for each GC/MS system utilized)

1. Bar graph spectrum

2. Mass listing

C. Blank Data

1. Tabulated results (Form I, Pages 1-4)

2. Tentatively Identified Compounds (TIC) (Form I, Part B) even if none found.

3. Raw Data - in order: VOA, BNA, Pesticida

a. Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS)

b. Chromatogram(s) and data system priorout(s) (GC)

c. HSL spectra with lab generated standard (dual display)

* data systems which are incapeble of dual diaplay shall provide spectra in order:

- raw HSL compound spectra
- enhanced or background subtracted spectra
- laboratory generated HSL standard spectra

d. GC/MS library search spectra for Tentatively Identified Compounds (TIC)

e. Quantitation/Calculatioo of Tentatively Identified Compound(s) (TIC) concantrations

D. Matrix Spike Data

1. Tabulated results (Form I, Pages 1-4)

2. Raw Data - in order: VOA, BNA, Pesticide

   a. Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS)

      - spectra not required

   b. Chromatogram(s) and data system printout(s) (GC)

      1. Both primary and confirmation column data is required.

E. Matrix Spike Duplicate Data

1. Tabulated results (Form I Pages 1-4)

2. Raw Data - in order: VOA, BNA, Pesticide

   a. Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS)

   b. Chromatogram(s) and data system printout(s) (GC)

      1. Both primary and confirmation column data is required.

CONTRACT REPORTING SCHEDULE

Report	No. Copies	Delivery Schedule	Report Distribution: SMO (1)	EMSL-LV (2)	Region-Client(3)	NEIC (4)
A. Weekly Progress Report	2	Weekly	X			
B. Sample Traffic Report	1	7 days from receipt of sample	X			
*C. Sample Data Package	3	40 days from receipt of sample	X	X	X	
*D. Raw QC Data Package	3	40 days from receipt of sample	X	X	X	
*E. Sample Data Summary Package	1	40 days from receipt of sample	X			
*F. Standards Data Package	3	40 days from receipt of sample	X	X	X	
G. GC/MS Tapes	Lot	Within 180 days after data submission Contractor requests PO for authorization to dispose of extracts or Within seven (7) days after receipt of written request by PO or SMO				
H. Extracts	Lot	Within 180 days after data submission Contractor requests PO for authorization to dispose of extracts or Within seven (7) days after receipt of written request by PO or SMO				
I. Complete Case File Purge	1 Pkg	180 days from date of data submission or within seven (7) days of written request by PO or SMO.				X

* Concurrent delivery required.

Figure 2.1. Contract reporting schedule.

SECTION III - FORM INSTRUCTION GUIDE

This section includes specific instructions for the completion of all required forms. These include instructions on header information as well as specific details to the bodies of individual forms. Instructions are arranged in the following order:

A. Organic Analysis Data Sheet (Form I)

B. Surrogate Percent Recovery Summary (Form II)

C. Matrix Spike/Matrix Spike Duplicate Summary (Form III)

D. Reagent Blank Summary (Form IV)

E. GC/MS Tuning and Calibration Standard (Form V)

F. Initial Calibration Data (Form VI)

G. Continuing Calibration Data (Form VII)

H. Pesticide/PCB Evaluation Standards Summary (Form VIII)

I. Pesticide/PCB Standards Summary (Form IX)

J. Pesticide/PCB Identification (Form X)

A. Organic Analysis Data Sheet (Form 1)

Part A - Organic Analysis Data Sheet

This form is used for tabulating and reporting sample analysis results for Hazardous Substance List (HSL) compounds. All four pages of the OADS (Form I) must be submitted for each sample, blank, matrix spike and matrix spike duplicate in a Case.

Complete the header information at the top of page one (1) including sample SMO number, contractor laboratory name, internal sample ID number, sample matrix, QC report number (if applicable), contract number and the date of sample receipt by the Contractor laboratory.

The Laboratory manager, or his designate, must sign the "Data Release Authorized By:" line in original signature. The signature indicates the laboratory manager or his designate has inspected the data package and it meets all the terms and conditions of the contract.

For each fraction (pages 1, 2 and 3), complete the section specific to each analysis (VOA, BNA, and Pesticide). Fill in SMO sample number in the box provided on each page. Indicate the concentration by circling either low or medium. Report the date the fraction was extracted/prepared, date analyzed and any concentration/dilution factor (if no concentration/dilution was required, this value should be one (1)). For soil samples, report the soil pH and percent moisture. (Soil samples that contain excess water which must be decanted prior to analysis will require a separate decanted percent moisture value.)

The date of sample receipt will be compared with the extraction/preparation and analysis dates of each fraction to assure that Contract holding times were not exceeded. The appropriate units, ug/L or ug/Kg, should be circled.

For identified HSL compounds, report the uncorrected (for blank) concentration as determined by the Laboratory. Report results to two significant figures using the rounding procedure described in Exhibit A.

Use the specific Data Reporting Qualifiers listed at the end of Form I. The Contractor is encouraged to use additional flags or footnotes. The definition of such flags must be explicit and such description attached to the end of Form I.

Part B - Tentatively Identified Compounds (Form I, Part B)

Fill in the SMO sample number in the box provided.

Report Tentatively Identified Compounds (TIC) including CAS number, compound name, fraction, scan number or retention time and the estimated concentration (criteria for reporting TIC in Exhibit D, Section IV). If in the opinion of the mass spectral specialist, no valid tentative identification can be made, the compound should be reported as unknown. Include a Form I,

Part B for every sample and reagent blank analyzed, even if none found. Mark the form "no volatile compounds found and/or no semi-volatile compounds found."

Peaks that are suspected as aldo-condensation reaction products should be summarized on Form I, Part B, footnoted as such, but not counted as part of the 20 most intense non-HSL compound requirements.

Sample Number

Organics Analysis Data Sheet
(Page 1)

Laboratory Name: _____ Case No: _____

Lab Sample ID No: _____ QC Report No: _____

Sample Matrix: _____ Contract No: _____

Data Release Authorized By: _____ Case Sample Received: _____

Volatile Compounds

Concentration: Low Medium (Circle One)

Date Extracted/Prepared: _____

Date Analyzed: _____

Conc/Dil Factor: _____ pH _____

Percent Moisture: _____

Percent Moisture (Decanted): _____

CAS Number		ug/l or ug/Kg (Circle One)
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	
156-60-5	Trans-1, 2-Dichloroethene	
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	

CAS Number		ug/l or ug/Kg (Circle One)
79-34-5	1, 1, 2, 2-Tetrachloroethane	
78-87-5	1, 2-Dichloropropane	
10061-02-6	Trans-1, 3-Dichloropropene	
79-01-6	Trichloroethene	
124-48-1	Dibromochloromethane	
79-00-5	1, 1, 2-Trichloroethane	
71-43-2	Benzene	
10061-01-5	cis-1, 3-Dichloropropene	
110-75-8	2-Chloroethylvinylether	
75-25-2	Bromoform	
591-78-6	2-Hexanone	
108-10-1	4-Methyl-2-Pentanone	
127-18-4	Tetrachloroethene	
108-88-3	Toluene	
108-90-7	Chlorobenzene	
100-41-4	Ethylbenzene	
100-42-5	Styrene	
	Total Xylenes	

Data Reporting Qualifiers

For reporting results to EPA, the following results qualifiers are used. Additional flags or footnotes explaining results are encouraged. However, the definition of each flag must be explained.

Values: If the result is a value greater than or equal to the detection limit, report the value.

U: Indicates compound was analyzed for but not detected. Report the minimum detection limit for the sample with the U (e.g. 10U) based on necessary concentration / dilution factors. (This is not necessarily the instrument detection limit.) The number should read: U- Compound was analyzed for but not detected. The number is the minimum detectable detection limit for the sample.

J: Indicates an estimated value. This flag is used either when calculating a concentration for tentatively identified compounds where a 1:1 response is assumed or when the mass spectral data indicates the presence of a compound that meets the identification criteria but the result is less than the specified detection limit but greater than zero (e.g. 45J).

C: This flag applies to pesticide parameters where the identification has been confirmed by GC/MS. (Single component pesticides 210 ng/ml in the final extract should be confirmed by GC/MS.)

B: This flag is used when the analyte is found in the blank as well as a sample. It indicates possible / probable blank contamination and warns the data user to take appropriate action.

Other: Other specific flags and footnotes may be required to properly define the results. If used, they must be fully described and such description attached to the data summary report.

Form I 1/85

Form I. Organics Analysis Data Sheet.

Laboratory Name _____

Case No _____

Sample Number

Organics Analysis Data Sheet
(Page 2)

Semivolatile Compounds

Concentration: Low Medium (Circle One)

Date Extracted/Prepared _____

Date Analyzed: _____

Conc/Dil Factor: _____

CAS Number		ug/l or ug/Kg (Circle One)
62-75-9	N-Nitrosodimethylamine	
108-95-2	Phenol	
62-53-3	Aniline	
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	
39638-32-9	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	Dimethyl Phthalate	
208-96-8	Acenaphthylene	
99-09-2	3-Nitroaniline	

CAS Number		ug/l or ug/Kg (Circle One)
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	
606-20-2	2,6-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	
92-87-5	Benzidine	
129-00-0	Pyrene	
85-68-7	Butylbenzylphthalate	
91-94-1	3,3'-Dichlorobenzidine	
56-55-3	Benzo(a)Anthracene	
117-81-7	bis(2-Ethylhexyl)Phthalate	
218-01-9	Chrysene	
117-84-0	Di-n-Octyl Phthalate	
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

Form I 1-85

Form I. (continued).

Laboratory Name _____

Case No _____

Sample Number

Organics Analysis Data Sheet
(Page 3)

Pesticide/PCBs

Concentration: Low Medium (Circle One)

Date Extracted/Prepared: _____

Date Analyzed _____

Conc/Dil Factor: _____

CAS Number		ug/l or ug/Kg (Circle One)
319-84-6	Alpha-BHC	
319-85-7	Beta-BHC	
319-86-8	Delta-BHC	
58-89-9	Gamma-BHC (Lindane)	
76-44-8	Heptachlor	
309-00-2	Aldrin	
1024-57-3	Heptachlor Epoxide	
959-98-8	Endosulfan I	
60-57-1	Dieldrin	
72-55-9	4,4'-DDE	
72-20-8	Endrin	
33213-65-9	Endosulfan II	
72-54-8	4,4'-DDD	
7421-93-4	Endrin Aldehyde	
1031-07-8	Endosulfan Sulfate	
50-29-3	4,4'-DDT	
72-43-5	Methoxychlor	
53494-70-5	Endrin Ketone	
57-74-9	Chlordane	
8001-35-2	Toxaphene	
12674-11-2	Aroclor-1016	
11104-28-2	Aroclor-1221	
11141-16-5	Aroclor-1232	
53469-21-9	Aroclor-1242	
12672-29-6	Aroclor-1248	
11097-69-1	Aroclor-1254	
11096-82-5	Aroclor-1260	

V_t = Volume of extract injected (ul)

V_o = Volume of water extracted (ml)

W_s = Weight of sample extracted (g)

V_t = Volume of total extract (ul)

V_o _____ or W_s _____ V_t _____ V_i _____

=

Form 1 1-85

Form I. (continued).

Laboratory Name: _____

Case No. _____

Sample Number

Organics Analysis Data Sheet
(Page 4)

Tentatively Identified Compounds

	CAS Number	Compound Name	Fraction	RT or Scan Number	Estimated Concentration (ug/l or ug/kg)
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.					

Form 1, Part B 1/85

Form I. (continued).

DATA REPORTING QUALIFIERS

For reporting results to the USEPA, the following contract specific qualifiers are to he used. The four qualffiers defined below are not subject to modification hy the laboratory. Additional flags or footnotes explaining results are anconraged. However, the definitioo of such flags or footnotes must be explicit.

Value - If the rasult is a value greater then or aqual to the detaction limit, report the valua.

U - Indicatee compound was analyzed for but not detected. Report the minimum derectioo limit for the sample with the U (a.g., 10U) baaed on necessary concentration/dilution actiona. (Thia is not necesaarily the instrument detection limit.) The footnote should read: U-Compound was analyzad for but nor detected. The number is the minimum attainable deraction limit for the aample.

J - Indicates ao astimated value. This flag is used either when astimaring a concentration for tentatively identified compounds where a 1:1 response is assumed or wheo the mass spectral dara indicares the presence of a compound ther meets the identification criteria but the result is less than the apecified detaction limit but greater then zero. (e.g., 10J)

C - This flag applies to pesticide parameters whera the identificarion has been confirmed by GC/MS. Single component pesticides $\geq$10 ng/ul in the final extract ahould be confirmed by GC/MS.

B - This flag is used when the analyte is found in rhe blank as well as a sample. It indicates possible/probable blank contamination and waros the data user to take appropriate action.

Other - Other specific flags and footnotes may be required to properly dafine the reaults. If used, they must be fully described and such descriprion attached to the data summary report.

Form I. (continued).

B. Water and Soil Surrogate Percent Recovery Summary (Form II)

These forms are used for reporting the Surrogate Spike Recovery (SSR) results for all samples, blanks, matrix spikes, and matrix spike duplicates (MS/MSD). Complete the header information including case number, laboratory contractor name, and contract number. Soil samples require a concentration level (low or medium). The laboratory must report all low concentration values on one form and medium level on a separate form. Do not mix low and medium samples.

Complete the data summary portion beginning with the Sample Management Office (SMO) traffic number. In order to facilitate computerized data entry, it is necessary to use the following sample suffixes:

XXXXX = SMO sample traffic number

XXXXXMS = indicates matrix spike sample

XXXXXMSD = indicates matrix spike duplicate sample

XXXXXRE = indicates reextracted sample

The laboratory must report all method blanks* on these forms. Each method blank (fraction specific) must be identified by the individual file ID (this number will be unique to each analysis, for each laboratory). The laboratory file ID will be the same used on the Reagent Blank Summary (Form IV) and the GC/MS Tuning and Calibration Standard (Form V). Report the laboratory file ID in the column marked SMO Traffic Number.

Use the following codes for individual surrogate fields:

(DL) = indicates no recovery values because surrogates were diluted out. Also, address in comments section of appropriate form.

(NR) = no value required. Use this code for fractions not required due to reanalysis or where SMO deleted a specific analysis (changes authorized by SMO in the IFB Protocol must be addressed in Case Narrative), or when more than one sample is used for the matrix spike/matrix spike duplicate analysis.

SSR results are recorded in the appropriate spaces and any results outside of QC recovery limits shall be annotated with an asterisk. The asterisked values are summarized at the bottom of the form. It is the contractor laboratory's responsibility to document reanalysis, or other corrective action taken when spike recovery values are outside of the contract required recovery limits.

Two columns on the form are provided to report optional surrogates if used.

*See Exhibit E, Part 3, for explanation of multiple method blanks.

WATER SURROGATE PERCENT RECOVERY SUMMARY

Case No. _____ Contract Laboratory _____ Contract No. _____

	VOLATILE			SEMI-VOLATILE								PESTICIDE
EPA SAMPLE NO.	TOLUENE-D8 (88-110)	BFB (86-115)	1,2 DICHLOROETHANE-D4 (72-120)	NITRO-BENZENE-D5 (54-120)	2-FLUORO-BIPHENYL (43-116)	TERPHENYL-D14 (33-141)			PHENOL-D6 (10-94)	2-FLUORO-PHENOL (21-100)	2,4,6 TRIBROMO-PHENOL (10-123)	DIBUTYL-CHLORENDATE** (50-150)

* VALUES ARE OUTSIDE OF CONTRACT REQUIRED QC LIMITS

** ADVISORY LIMITS ONLY

Volatiles _____ out of _____ ; outside of QC limits

Semi-Volatiles _____ out of _____ ; outside of QC limits ;

Pesticides _____ out of _____ ; outside of QC limits

Comments: _____

FORM II

SOIL SURROGATE PERCENT RECOVERY SUMMARY

Case No. _____ Contract Laboratory _____ Contract No. _____

Low _____ Medium _____

	VOLATILE				SEMI-VOLATILE							PESTICIDE
SMO TRAFFIC NO.	TOLUENE-D8 (88-110)	BFB (86-115)	1,2 DICHLOROETHANE-D4 (76-114)	NITROBENZENE-D5 (23-120)	2-FLUOROBIPHENYL (30-115)	TERPHENYL-D14 (18-137)			PHENOL-D5 (24-113)	2-FLUOROPHENOL (25-121)	2,4,6 TRIBROMOPHENOL (19-122)	DIBUTYLCHLORENDATE ** (20-150)

* VALUES ARE OUTSIDE OF CONTRACT REQUIRED QC LIMITS

** ADVISORY LIMITS ONLY

Volatiles: _____ out of _____ outside of QC limits

Semi-Volatiles: _____ out of _____ outside of QC limits

Pesticides: _____ out of _____ outside of QC limits

Comments: _____

FORM II

C. Matrix Spike/Matrix Spike Duplicate Recovery Summary (Form III)

This form is used for reporting matrix spike and matrix spike duplicate (MS/MSD) percent recovery results and the relative percent difference (RPD) between the two analyses.

Complete the header information including Case number, contractor laboratory name, contract number, units, and level of analysis for soil/sediment samples. Since MS/MSD analysis is required per matrix type (water or soil), concentration level, and number of samples, it is necessary to complete this form for every MS/MSD analysis performed (see Exhibit E). List the SMO sample number used for each fraction (The same sample should be used for all fractions if sufficient sample is available. If not available, it is permissible to do a MS/MSD per fraction VOA, BNA, Pesticide.) When more than one sample is used to perform the MS/MSD analysis, report the surrogate spike information on the Surrogate Spike Percent Recovery Summary (Form II) by fraction (specify the SMO sample number used for each fraction and the surrogte recovery information for that sample and fraction.

Report the amount of matrix spike spiking solution added in ug/L or ug/Kg in the column marked "Conc Spike added."

Report sample results for all matrix spike compounds. If a matrix spike compound was not detected during sample analyses, enter a zero (0) for that compound in the column marked "Sample Result." Calculate and report the concentration and percent recovery (see Exhibit E) for each spiking compound in the matrix spike sample and the matrix spike duplicate sample. Calculate and report the relative percent difference (RPD) (see Exhibit E) between the matrix spike and matrix spike duplicate. Asterisk and summarize all values outside of QC advisory limits.

Although no further action is required from the Contractor Laboratory, the percent recovery and RPD values will be used to update present performance-based QC limits. Comment as necessary at the bottom of the form.

WATER MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Case No. _____ Contractor _____ Contract No. _____

FRACTION	COMPOUND	CONC. SPIKE ADDED (ug/L)	SAMPLE RESULT	CONC. MS	% REC	CONC. MSD	% REC	RPD	QC LIMITS* RPD	QC LIMITS* RECOVERY
VOA SMO SAMPLE NO. _____	1,1-Dichloroethene								14	61-145
	Trichloroethene								14	71-120
	Chlorobenzene								13	75-130
	Toluene								13	76-125
	Benzene								11	76-127
B/N SMO SAMPLE NO. _____	1,2,4-Trichlorobenzene								28	39-98
	Acenaphthene								31	46-118
	2,4 Dinitrotoluene								38	24-96
	Di-n-Butylphthalate								40	11-117
	Pyrene								31	26-127
	N-Nitroso-Di-n-Propylamine								38	41-116
	1,4-Dichlorobenzene								28	28-97
ACID SMO SAMPLE NO. _____	Pentachlorophenol								50	9-103
	Phenol								42	12-89
	2-Chlorophenol								40	27-123
	4-Chloro-3-Methylphenol								42	23-97
	4-Nitrophenol								50	10-80
PEST SMO SAMPLE NO. _____	Lindane								15	56-123
	Heptachlor								20	40-131
	Aldrin								22	40-120
	Dieldrin								18	52-126
	Endrin								21	56-121
	4,4'-DDT								27	38-127

*ASTERISKED VALUES ARE OUTSIDE QC LIMITS.

RPD: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

RECOVERY: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

Comments: _____

FORM III 1/85

Form III. MS/MSD Results (water).

SOIL MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Case No. _____ **Contractor** _____ **Contract No.** _____

Low Level _____ **Medium Level** _____

FRACTION	COMPOUND	CONC. SPIKE ADDED (ug/Kg)	SAMPLE RESULT	CONC. MS	% REC	CONC. MSD	% REC	RPD	QC LIMITS * RPD	QC LIMITS * RECOVERY
VOA SMO SAMPLE NO. _____	1,1-Dichloroethene								22	59-172
	Trichloroethene								24	62-137
	Chlorobenzene								21	60-133
	Toluene								21	59-139
	Benzene								21	66-142
B/N SMO SAMPLE NO. _____	1,2,4-Trichlorobenzene								23	38-107
	Acenaphthene								19	31-137
	2,4-Dinitrotoluene								47	28-89
	Di-n-Butylphthalate								47	29-135
	Pyrene								36	35-142
	N-Nitroso-di-n-Propylamine								38	41-126
	1,4-Dichlorobenzene								27	28-104
ACID SMO SAMPLE NO. _____	Pentachlorophenol								47	17-109
	Phenol								35	26-90
	2-Chlorophenol								50	25-102
	4-Chloro-3-Methylphenol								33	26-103
	4-Nitrophenol								50	11-114
PEST SMO SAMPLE NO. _____	Lindane								50	46-127
	Heptachlor								31	35-130
	Aldrin								43	34-132
	Dieldrin								38	31-134
	Endrin								45	42-139
	4,4'-DDT								50	23-134

*ASTERISKED VALUES ARE OUTSIDE QC LIMITS

RPD: VOAs ____ out of ____ ; ____ outside QC limits
B/N ____ out of ____ ; ____ outside QC limits
ACID ____ out of ____ ; ____ outside QC limits
PEST ____ out of ____ ; ____ outside QC limits

RECOVERY: VOAs ____ out of ____ ; ____ outside QC limits
B/N ____ out of ____ ; ____ outside QC limits
ACID ____ out of ____ ; ____ outside QC limits
PEST ____ out of ____ ; ____ outside QC limits

Comments: _____

FORM III 1/85

Form III. MS/MSD Results (soil).

D. Reagent Blank Summary (Form IV)

This form is used to report the concentrations of both HSL and non-HSL compounds detected in the laboratory reagent blank(s).

The laboratory should complete all the header information including Laboratory name, Case number, contract number, sample matrix and concentration level. Since the protocol requires a reagent blank for each sample matrix (water or soil) and concentration level (low or medium soil), the laboratory must ensure the proper number of reagent blank summaries are included.

The laboratory should list compounds (HSL or non-HSL) by order of fractions: VOA, BNA, Pesticide. Since a VOA blank is required each 12 hours volatile analysis is performed, compounds should be separated as Method Blank 1, Method Blank 2, etc. The laboratory should only report pesticides/PCBs detected in the reagent blank that meet the identification criteria (second column confirmation) specified in Exhibit E.

The laboratory should complete the columns for concentration, contract required detection limits (where applicable) and CAS number. Tentatively identified compounds (TIC) reported, must follow the identification criteria ourlined in (Exhibit D). Compound spectra that fail the qualitative identification criteria must be labeled as "unknown".

Sample concentration data are to be reported uncorrected for blank values. The laboratory must ensure that the proper number of reagent blank analyses are performed. EPA data evaluators and/or data auditors will perform blank corrections on an as needed basis.

REAGENT BLANK SUMMARY

Case No. _____ Contractor _____ Contract No. _____

FILE ID	DATE OF ANALYSIS	FRACTION	MATRIX	CONC LEVEL	INST. ID	CAS NUMBER	COMPOUND NAME (For all processes)	CONC.	UNITS	CONC.

Comments:

FORM IV

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Reagent Blank Summary

E. GC/MS Tuning and Calibration Standard (Form V)

This form serves two distinct purposes. The USEPA wil use this form to verify that a Contract Laboratory's GC/MS system(s) meet the required tuning criteria for both DFTPP and BFB and also as a summary of all samples, standards, blanks, matrix spikes, and matrix spike duplicates analyzed under a specific tune.

The Laboratory must complete all header information including: laboratory name, Case number, Contract number, instrument ID, and data and time of analysis on each DFTPP and/or BFB calibration standard form submitted.

Using the mass listing for either DFTPP and/or BFB, the Contractor must fill in all required ion abundances. Report all values to three significent figures. For rounding rules, follow the EPA Handbook of Analytical Quality Control in Water and Wasteweter Laboratories (EPA-600/4-79-019). Calculate and report ion abundance ratios specified by parentheses.

To complete the bottom of Form V, the laboratory must summarise each sample, standard, blank, MS and MSD analyzed under the specific tune. List in chronological order, including SMO sample number, laboratory ID (for standards/ blanks), and date/time of analysis (report time in military format: 3:10 p.m. = 1510 hours).

The Laboratory Manager, or his designate, must sign in original signature the "Data Release Authorized By:" line. The Laboratory Manager's signature indicates that he or his designate has reviewed the data and has determined that the data meets all terms and conditions of the contract (i.e., tuning criteria met). The EPA may use non-compliant tunes as the basis for non-payment of all affected sample fractions.

GC/MS TUNING AND MASS CALIBRATION
Decafluorotriphenylphosphine (DFTPP)

Case No. _____ Contractor _____ Contract No. _____

Instrument ID _____ Date _____ Time _____

Lab ID _____ Date Release Authorized By: _____

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 - 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 in parenthesis is % mass 69.
[2] Value in parenthesis is % mass 442.

THIS PERFORMANCE TUNE APPLIES TO THE FOLLOWING SAMPLES, BLANKS AND STANDARDS.

SAMPLE ID	LAB ID	DATE OF ANALYSIS	TIME OF ANALYSIS

4/84

FORM V

Form V. DFTPP Tuning and Mass Calibration.

GC/MS TUNING AND MASS CALIBRATION

Bromofluorobenzene (BFB)

Case No. _____ Contractor _____ Contract No. _____

Instrument ID _____ Date _____ Time _____

Lab ID _____ Data Release Authorized By: _____

m/e	ION ABUNDANCE CRITERIA	%RELATIVE ABUNDANCE
50	15.0 - 40.0% of the base peak	
75	30.0 - 60.0% of the base peak	
95	Base peak, 100% relative abundance	
96	5.0 - 9.0% of the base peak	
173	Less than 1.0% of the base peak	
174	Greater than 50.0% of the base peak	
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 in parenthesis is % mass 174.
[2]Value in parenthesis is % mass 176.

THIS PERFORMANCE TUNE APPLIES TO THE FOLLOWING SAMPLES, BLANKS AND STANDARDS.

SAMPLE ID	LAB ID	DATE OF ANALYSIS	TIME OF ANALYSIS

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FORM V

Form V. BFB Tuning and Mass Calibration.

F. Initial Calibration Data (Form VI)

This form must be completed each time a Contractor laboratory's GC/MS must undergo initial calibration for either volatile or semi-volatile HSL compounds, and submitted with each appropriate Case.

After a GC/MS system has undergone an initial 5 point* 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 semi-volatile HSL initial calibration performed.

The laboratory must complete all header information including: SMO Case number, Contract number, laboratory name, instrument ID, date of analysis and laboratory ID for each standard. The laboratory must fill out and complete the response factor data for the five calibration points, and then calculate and report the average response factor ($\overline{RF}$) for all HSL compounds. The laboratory must calculate the %RSD for all CCC compounds. After ensuring all CCC compounds have a %RSD of less than 30 percent, calculate and report %RSD for all other HSL compounds. The USEPA plans to use this data to develop performance based criteria in the future.

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

where

RSD = Relative Standard Deviation

SD = Standard Deviation of initial 5 response factors (per compound)

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

$\bar{x}$ = mean of inirial 5 response factors (per compound)

*Note: The nine compounds listed in Exhibit E, Part 2 will only require a four point initial calibration due to the higher Contract Required Detection Limits (CRDL) for these compounds. Benzidine only requires a three-point calibration at 80, 120 and 160 total nanograms.

Initial Calibration Data
Volatile HSL Compounds

Case No: _____ Instrument I.D: _____

Contractor: _____ Calibration Date: _____

Contract No: _____

Minimum RF for SPCC is 0.300 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{100}	RF_{150}	RF_{200}	RF	% RSD	CCC-SPCC--
Chloromethane								* *
Bromomethane								
Vinyl Chloride								*
Chloroethane								
Methylene Chloride								
Acetone								
Carbon Disulfide								
1, 1-Dichloroethene								*
1, 1-Dichloroethane								* *
Trans-1, 2-Dichloroethene								
Chloroform								*
1, 2-Dichloroethane								
2-Butanone								
1, 1, 1-Trichloroethane								
Carbon Tetrachloride								
Vinyl Acetate								
Bromodichloromethane								
1, 2-Dichloropropene								*
Trans-1, 3-Dichloropropene								
Trichloroethene								
Dibromochloromethane								
1, 1, 2-Trichloroethane								
Benzene								
cis-1, 3-Dichloropropene								
2-Chloroethylvinylether								
Bromoform								* *
2-Hexanone								
4-Methyl-2-Pentanone								
Tetrachloroethene								
1, 1, 2, 2-Tetrachloroethane								* *
Toluene								*
Chlorobenzene								* *
Ethylbenzene								*
Styrene								
Total Xylenes								

RF -Response Factor (substitute in the amount of ug/L)
RF -Average Response Factor
%RSD -Percent Relative Standard Deviation

CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)

Form VI

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Form VI. Initial Calibration - Volatile HSL Compounds

Initial Calibration Data
Semivolatile HSL Compounds
(Page 1)

Case No: _____ Instrument ID. _____

Contractor: _____ Calibration Date. _____

Contract No. _____

Minimum $\overline{RF}$ for SPCC is 0.050 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	% RSD	CCC* SPCC**
N-Nitrosodimethylamine								
Phenol								*
Aniline								
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	†							
Dimethyl Phthalate								
Acenaphthylene								
3-Nitroaniline	†							
Acenaphthene								*
2,4-Dinitrophenol	†							* *
4-Nitrophenol	†							* *
Dibenzofuran								

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ - Average Response Factor
%RSD - Percent Relative Standard Deviation
CCC - Calibration Check Compounds (*)

SPCC - System Performance Check Compounds (**)
† - Not detectable at 20 ng for benzoic
not detectable at < 80 ng

Form VI

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Form VI. Initial Calibration - Semi-Volatile HSL Compounds

Initial Calibration Data
Semivolatile HSL Compounds
(Page 2)

Case No: _____ Instrument ID: _____

Contractor: _____ Calibration Date: _____

Contract No: _____

Minimum $\overline{RF}$ for SPCC is 0.050 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	% RSD	CCC-SPCC--
2,4-Dinitrotoluene								
2,6-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								
Fluoranthene								*
Benzidine	†	†						
Pyrene								
Butylbenzylphthalate								
3,3'-Dichlorobenzidine								
Benzo(a)Anthracene								
bis(2-Ethylhexyl)Phthalate								
Chrysene								
Di-n-Octyl Phthalate								*
Benzo(b)Fluoranthene								
Benzo(k)Fluoranthene								
Benzo(a)Pyrene								*
Indeno(1,2,3-cd)Pyrene								
Dibenz(a,h)Anthracene								
Benzo(g,h,i)Perylene								

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (+)
SPCC -System Performance Check Compounds (++)
† -Not detectable at 20 ng for benzidine
not detectable at < 80 ng
(1) -Cannot be separated from diphenylamine

Form VI

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Form VI. Initial Calibration - Semi-Volatile HSL Compounds

G. 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 semi-volatile HSL 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 is completed and submitted.

The Contractor laboratory must complete all header information including: SMO Case number, Laboratory name, Contract number, instrument ID, date and time of analysis and date of initial calibration. Using the appropriate Initial Calibration (Volatile and/or Semi-volatile) fill in the average response factor ($\overline{RF}$) for each HSL compound. Report the response factor from the calibration standard analysis. Calculate the Percent Difference (%D) for all CCC compounds and ensure that the %D is less than 25 percent. After this criteria has been met, report the Percent Difference for all HSL compounds. Submit a properly completed form for each twelve (12) hours for both Volatile and Semi-volatile HSL compound analysis.

$$\% \text{ Difference} = \frac{\overline{RF_I} - RF_c}{\overline{RF_I}} \times 100$$

where,

$\overline{RF_I}$ = average response factor from initial calibration.

RF_c = response factor from current verification check standard.

Continuing Calibration Check
Volatile HSL Compounds

Case No: _____ Calibration Date: _____

Contractor: _____ Time: _____

Contract No: _____ Laboratory ID: _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.300 Maximum %D for CCC is 25%

Compound	RF	RF_{50}	%D	CCC	SPCC
Chloromethane					* *
Bromomethane					
Vinyl Chloride				*	
Chloroethane					
Methylene Chloride					
Acetone					
Carbon Disulfide					
1, 1-Dichloroethene				*	
1, 1-Dichloroethane					* *
Trans-1, 2-Dichloroethene					
Chloroform				*	
1, 2-Dichloroethane					
2-Butanone					
1, 1, 1-Trichloroethane					
Carbon Tetrachloride					
Vinyl Acetate					
Bromodichloromethane					
1, 2-Dichloropropane				*	
Trans-1, 3-Dichloropropene					
Trichloroethene					
Dibromochloromethane					
1, 1, 2-Trichloroethane					
Benzene					
cis-1, 3-Dichloropropene					
2-Chloroethylvinylether					
Bromoform					* *
2-Hexanone					
4-Methyl-2-Pentanone					
Tetrachloroethene					
1, 1, 2, 2-Tetrachloroethane					* *
Toluene				*	
Chlorobenzene					* *
Ethylbenzene				*	
Styrene					
Total Xylenes					

RF_{50} -Response Factor from daily standard (40 or 50 ug/l
RF -Average Response Factor from initial calibration Form VI

%D -Percent Difference
CCC -Calibration Check Compounds (*)
SPCC -Stream Performance Check Compounds (**)

Form VII

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Form VII. Continuing Calibration Data - Volatiles

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 1)

Case No. _____ Calibration Date. _____

Contractor. _____ Time: _____

Contract No. _____ Laboratory ID. _____

Instrument ID. _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	RF	RF_{50}	%D	CCC	SPCC
N-Nitrosodimethylamine					
Phenol				*	
Aniline					
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 †					
Dimethyl Phthalate					
Acenaphthylene					
3-Nitroaniline †					
Acenaphthene				*	
2, 4 Dinitrophenol †					* *
4-Nitrophenol †					* *
Dibenzofuran					

RF_{50} - Response Factor from daily standard file at concentration indicated (50 total nanograms)

RF - Average Response Factor from initial calibration Form VI

%D - Percent Difference

CCC - Calibration Check Compounds (*)

SPCC - System Performance Check Compounds (* *)

† - Due to low response analysis at 50 total nanograms

Form VII. Continuing Calibration Data - Semi-Volatiles

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 2)

Case No: _____ Calibration Date _____

Contractor: _____ Time: _____

Contract No: _____ Laboratory ID: _____

Instrument ID: _____ Initial Calibration Date _____

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	RF	RF_{50}	% D	CCC	SPCC
2,4-Dinitrotoluene					
2,6-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					
Fluoranthene				*	
Benzidine †					
Pyrene					
Butylbenzylphthalate					
3,3'-Dichlorobenzidine					
Benzo(a)Anthracene					
bis(2-Ethylhexyl)Phthalate					
Chrysene					
Di-n-Octyl Phthalate				*	
Benzo(b)Fluoranthene					
Benzo(k)Fluoranthene					
Benzo(a)Pyrene				*	
Indeno(1,2,3-cd)Pyrene					
Dibenz(a,h)Anthracene					
Benzo(g,h,i)Perylene					

RF_{50} -Response Factor from daily standard for at concentration indicated (50 total nanograms)

RF -Average Response Factor from initial calibration Form VI

%D -Percent Difference

† -Due to low response analysis on 50 total nanograms

CCC -Calibration Check Compounds (*)

SPCC -System Performance Check Compounds (*)

(1) -Cannot be separated from diphenylamine

Form VII

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Form VII. Continuing Calibration Data - Semi-Volatiles

E. Pesticide Evaluation Standards Summary (Form VIII)

This form is used to report all of the twenty-four (24) hour requirements during pesticide analysis.

The laboratory should complete all the header information including Laboratory name, Case number, Contract number, date of analysis, GC column and GC instrument identification.

Evaluation Standard Mix A, B, and C must be analyzed every 24 hours to check the linearity of the GC system. Calculate and report the Calibration Factor (total peak area/amount injected in nanograms) for each of the four pesticides (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. The RSD must be less than 10 percent for Aldrin, Endrin, and Dibutylchlorendate. If the %RSD for 4,4'-DDT exceeds 10 percent, see Exhibit E, part 7, paragraph 7.5.4.1.

$$\%RSD = \frac{SD}{\bar{X}} \times 100 \qquad \text{Eq. 1.1}$$

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

$\bar{X}$ = mean of initial three Calibration factors (per compound)

Evaluation Standard Mix B must be analyzed after every ten samples during a twenty-four period. Calculate and report the percent breakdown for 4,4'-DDT and/or Endrin for the mixed phase GC column (see Exhibit E). Enter results in appropriate columns. Provide the laboratory identification and time of analysis, for each analysis of the Evaluation Standard Mix B.

$$\%\ \text{breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100 \qquad \text{Eq. 1.2}$$

$$\%\ \text{breakdown for Endrin} = \qquad \text{Eq. 1.3}$$

$$\frac{\text{Total Endrin degradation peak areas (Endrin Aldehyde + Endrin Ketone)}}{\text{Total Endrin Peak Area (Endrin + Endrin Aldehyde + Endrin Ketone)}} \times 100$$

Note: The term peak height may be substituted for the term peak area.

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 percent breakdown must not exceed 20 percent for Endrin or 4,4'-DDT.

If there is evidence of a peak at the retention time of 4,4'-DDD/Endrin aldehyde (which co-elute on the OV-1 GC column), calculate a combined percent breakdown for Endrin/4,4'-DDT using Equation 1.4. The combined degradation must not exceed 20 percent.

$$\text{Combined \% Breakdown} = \frac{\text{Total Endrin/DDT degradation peak area (DDD, DDE, Endrin Aldehyde, Endrin Ketone)}}{\text{Total Endrin/DDT peak area (Endrin, Endrin Aldehyde, Endrin Ketone, DDD, DDE, DDT)}} \qquad \text{Eq. 1.4}$$

Every standard, sample, and blank must contain the surrogate Dibutylchlorendate at the specified level for both water and/or soil/sediment samples. The retention time shift for Dibutylchlorendate on packed columns must not exceed 2 percent (0.3 percent for capillary columns) difference (%D) between the initial standard (Evaluation Standard Mix A) and any sample analyzed during the 12 hour time period. Calculate and report the percent difference (%D) for all samples, standards and blanks. Fill in SMO sample number, Laboratory ID and time of analysis for each sample and blank.

$$\text{\% Difference} = \frac{RT_i - RT_s}{RT_i} \times 100 \qquad \text{Eq 1.5}$$

where RT_i = absolute retention time of dibutylchorendate in the initial standard (Evaluation Mixture A).

RT_s = absolute retention time of dibutylchlorendate in the sample, blank, or any standard analyzed after Evaluation Mixture A.

Form VIII is required for each twenty-four (24) hour period, for each GC system and for each GC column used to analyze RSL Pesticide/PCBs.

Note: The term peak height may be substituted for the term peak area.

Pesticide Evaluation Standards Summary

Case No. _____ Laboratory _____

Contract No. _____ GC Column _____

Date of Analysis _____ Instrument ID _____

EVALUATION CHECK FOR LINEARITY

LABORATORY ID				
PESTICIDE	CALIBRATION FACTOR EVAL. MIX A	CALIBRATION FACTOR EVAL. MIX B	CALIBRATION FACTOR EVAL. MIX C	% RSD (≤10%)
ALDRIN				
ENDRIN				
4,4'-DDT(1)				
DIBUTYL CHLORENDATE				

EVALUATION CHECK FOR 4,4'-DDT/ENDRIN BREAKDOWN

	PERCENT BREAKDOWN EXPRESSED AS TOTAL DEGRADATION			
	EVAL. MIX B	EVAL. MIX B	EVAL. MIX B	EVAL. MIX B
LABORATORY ID				
TIME OF ANALYSIS				
ENDRIN				
4,4'-DDT				
COMBINED(2)				

EVALUATION OF RETENTION TIME SHIFT FOR DIBUTYLCHLORENDATE

SMO SAMPLE NO.	LAB ID	TIME OF ANALYSIS	PERCENT DIFF.	SMO SAMPLE NO.	LAB ID	TIME OF ANALYSIS	PERCENT DIFF.

(1) SEE EXHIBIT E, SECTION 7.5.4

(2) SEE EXHIBIT E, SECTION 7.3.1.2.2.1

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FORM VIII

Form VIII. Pesticide Evaluation Standards Data.

1. Pesticide/PCB Standards Summary (Form IX)

This form is used to monitor the variation in the Calibration Factor for each pesticide standard during the twelve (12) hour period.

The laboratory should complete the header information including the SMO Case number, Laboratory name, and Contract number. This form is required for each twelve hours, for each GC system and for each GC column used to analyze HSL Pesticides/PCBs.

Individual Standard Mix A or B must be analyzed at or near the beginning of a twelve hour period and again at the end. Enter the date of analysis and time of analysis (in Military time) in the appropriate spaces for each of the two analyses. Calculate and report the retention time (RT) and retention time window for each compound in Individual Standard Mix A or B (see Exhibit E, Section III, Part 7). Calculate the Calibration Factor for each compound using Equation 1.5 and report results on the appropriate column.

$$\text{Calibration Factor} = \frac{\text{Total peak area of a Standard}}{\text{Total mass injected (ng)}} \qquad \text{Eq 1.5}$$

At the end of the 12 hour period calculate and report the percent difference in the Calibration Factor for each pesticide using Equation 1.6.

$$\text{Percent Difference (\%D)} = \frac{Ab_1 - Ab_2}{Ab_1} \times 100 \qquad \text{Eq. 1.6}$$

where,

Ab_1 = Calibration Factor from the initial standard

Ab_2 = Calibration Factor from the standard at the end of the 12 hour period.

The percent difference between the individual Calibration Factors for each compound in the pesticide standard may vary no more than 15 percent during a twelve hour quantitation run, nor more than 20 percent during a twelve hour confirmation run.

The Laboratory is required to provide alpha and gamma-chlordane data only for "weathered" chlordane samples as described in Exhibit D, Section IV.

Note: The term peak height may be substituted for the term peak area.

PESTICIDE/PCB STANDARDS SUMMARY

Case No. _____ Laboratory _____

Contract No. _____ GC Column _____ GC Instrument ID _____

	DATE OF ANALYSIS _____ TIME OF ANALYSIS _____ LABORATORY ID _____				DATE OF ANALYSIS _____ TIME OF ANALYSIS _____ LABORATORY ID _____			
COMPOUND	RT	RETENTION TIME WINDOW	CALIBRATION FACTOR	CONF. OR QUANT.	RT	CALIBRATION FACTOR	CONF. OR QUANT.	PERCENT DIFF.**
alpha-BHC								
beta-BHC								
delta-BHC								
gamma-BHC								
Heptachlor								
Aldrin								
Heptachlor Epoxide								
Endosulfan I								
Dieldrin								
4,4'-DDE								
Endrin								
Endosulfan II								
4,4'-DDD								
Endrin Aldehyde								
Endosulfan Sulfate								
4,4'-DDT								
Methoxychlor								
Endrin Ketone								
Tech. Chlordane								
alpha-Chlordane*								
gamma-Chlordane*								
Toxaphene								
Aroclor - 1016								
Aroclor - 1221								
Aroclor - 1232								
Aroclor - 1242								
Aroclor - 1248								
Aroclor - 1254								
Aroclor - 1260								

* SEE EXHIBIT E, PART 7

** CONF. = CONFIRMATION (<20% DIFFERENCE)
QUANT. = QUANTITATION (<15% DIFFERENCE)

FORM IX

J. Pesticide/PCB Identification (Form X)

This form summarizes all identification/confirmation of all pesticides/PCBs in a specific Case.

The Laboratory should complete all the header information including SMO Case number, Laboratory name and Contract number. For each pesticide/PCB identified and confirmed, complete the appropriate columns for SMO sample number, primary column used, pesticide/PCB identified, run number from chromatogram, retention time of tentative ID, retention time window of the appropriate standard, confirmation column type, retention time on confirmatory column and retention time window of the appropriate standard on confirmatory column.

The last column refers to confirmation by GC/MS. This column is completed with either a Y or N.

This form need not be submitted if there are no positive results for pesticides/PCBs. It must be submitted if there are any samples positive for pesticides or PCBs.

Pesticide/PCB Identification

Case No. _____ Laboratory _____

Contract No. _____

SAMPLE ID	PRIMARY COLUMN	PESTICIDE/ PCB	RT OF TENTATIVE ID	RT WINDOW OF APPROPRIATE STANDARD	CONFIRMATION COLUMN	RT ON CONFIRMATORY COLUMN	RT WINDOW OF APPROPRIATE STANDARD	GC/MS CONFIRMED (Y or N)

4/84

FORM X

Form X. Pesticide/PCB Identification.

EXHIBIT C

Hazardous Substance List (HSL) and

Contract Required Detection Limits (CRDL)

EXHIBIT C

Hazardous Substance List (HSL) and
Contract Required Detection Limits (CRDL)**

Volatiles	CAS Number	Detection Limits[A] Low Water[B] ug/L	Low Soil/Sediment[C] 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	75-35-3	5	5
10. trans-1,2-Dichloroethene	156-60-5	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. 1,1,2,2-Tetrachloroethane	79-34-5	5	5
19. 1,2-Dichloropropane	78-87-5	5	5
20. trans-1,3-Dichloropropene	10061-02-6	5	5
21. Trichloroethene	79-01-6	5	5
22. Dibromochloromethane	124-48-1	5	5
23. 1,1,2-Trichloroethane	79-00-5	5	5
24. Benzene	71-43-2	5	5
25. cis-1,3-Dichloropropene	10061-01-5	5	5

(continued)

Volatiles	CAS Number	Detection Limits* Low Water[a] ug/L	Low Soil/Sediment[b] ug/Kg
26. 2-Chloroethyl Vinyl Ether	110-75-8	10	10
27. Bromoform	75-25-2	5	5
28. 2-Hexanone	591-78-6	10	10
29. 4-Methyl-2-pentanone	108-10-1	10	10
30. Tetrachloroethene	127-18-4	5	5
31. Toluene	108-88-3	5	5
32. Chlorobenzene	108-90-7	5	5
33. Ethyl Benzene	100-41-4	5	5
34. Styrene	100-42-5	5	5
35. Total Xylenes		5	5

[a]Medium Water Contract Required Detection Limits (CRDL) for Volatile HSL Compounds are 100 times the individual Low Water CRDL.

[b]Medium Soil/Sediment Contract Required Detection Limits (CRDL) for Volatile HSL Compounds are 100 times the individual Low Soil/Sediment CRDL.

Semi-Volatiles	CAS Number	Detection Limits* Low Water[c] ug/L	Low Soil/Sediment[d] ug/Kg
36. N-Nitrosodimethylamine	62-75-9	10	330
37. Phenol	108-95-2	10	330
38. Aniline	62-53-3	10	330
39. bis(2-Chloroethyl) ether	111-44-4	10	330
40. 2-Chlorophenol	95-57-8	10	330
41. 1,3-Dichlorobenzene	541-73-1	10	330
42. 1,4-Dichlorobenzene	106-46-7	10	330
43. Benzyl Alcohol	100-51-6	10	330
44. 1,2-Dichlorobenzene	95-50-1	10	330
45. 2-Methylphenol	95-48-7	10	330
46. bis(2-Chloroisopropyl) ether	39638-32-9	10	330
47. 4-Methylphenol	106-44-5	10	330
48. N-Nitroso-Dipropylamine	621-64-7	10	330
49. Hexachloroethane	67-72-1	10	330
50. Nitrobenzene	98-95-3	10	330
51. Isophorone	78-59-1	10	330
52. 2-Nitrophenol	88-75-5	10	330
53. 2,4-Dimethylphenol	105-67-9	10	330
54. Benzoic Acid	65-85-0	50	1600
55. bis(2-Chloroethoxy) methane	111-91-1	10	330
56 2,4-Dichlorophenol	120-83-2	10	330
57. 1,2,4-Trichlorobenzene	120-82-1	10	330
58. Naphthalene	91-20-3	10	330
59. 4-Chloroaniline	106-47-8	10	330
60. Hexachlorobutadiene	87-68-3	10	330
61. 4-Chloro-3-methylphenol (para-chloro-meta-cresol)	59-50-7	10	330
62. 2-Methyloaphthalene	91-57-6	10	330
63. Hexachlorocyclopentadiene	77-47-4	10	330
64. 2,4,6-Trichlorophenol	88-06-2	10	330
65. 2,4,5-Trichlorophenol	95-95-4	50	1600

(continued)

Semi-Volatiles	CAS Number	Detection Limits* Low Water[c] ug/L	Low Soil/Sediment[d] ug/Kg
66. 2-Chloronaphthalene	91-58-7	10	330
67. 2-Nitroaniline	88-74-4	50	1600
68. Dimethyl Phthalate	131-11-3	10	330
69. Acenaphthylene	208-96-8	10	330
70. 3-Nitroaniline	99-09-2	50	1600
71. Acenaphthene	83-32-9	10	330
72. 2,4-Dinitrophenol	51-28-5	50	1600
73. 4-Nitrophenol	100-02-7	50	1600
74. Dibenzofuran	132-64-9	10	330
75. 2,4-Dinitrotoluene	121-14-2	10	330
76. 2,6-Dinitrotoluene	606-20-2	10	330
77. Diethylphthalate	84-66-2	10	330
78. 4-Chlorophenyl Phenyl ether	7005-72-3	10	330
79. Fluorene	86-73-7	10	330
80. 4-Nitroaniline	100-01-6	50	1600
81. 4,6-Dinitro-2-methylphenol	534-52-1	50	1600
82. N-nitrosodiphenylamine	86-30-6	10	330
83. 4-Bromophenyl Phenyl ether	101-55-3	10	330
84. Hexachlorobenzene	118-74-1	10	330
85. Pentachlorophenol	87-86-5	50	1600
86. Phenanthrene	85-01-8	10	330
87. Anthracene	120-12-7	10	330
88. Di-n-butylphthalate	84-74-2	10	330
89. Fluoranthene	206-44-0	10	330
90. Benzidine	92-87-5	80	2600
91. Pyrene	129-00-0	10	330
92. Butyl Benzyl Phthalate	85-68-7	10	330
93. 3,3'-Dichlorobenzidine	91-94-1	20	660
94. Benzo(a)anthracene	56-55-3	10	330
95. bis(2-ethylhexyl)phthalate	117-81-7	10	330
96. Chrysene	218-01-9	10	330
97. Di-n-octyl Phthalate	117-84-0	10	330
98. Benzo(b)fluoranthene	205-99-2	10	330
99. Benzo(k)fluoranthene	207-08-9	10	330
100. Benzo(a)pyrene	50-32-8	10	330

(continued)

Semi-Volatiles	CAS Number	Detection Limits* Low Water[c] ug/L	Low Soil/Sediment[d] ug/Kg
101. Indeno(1,2,3-cd)pyrene	193-39-5	10	330
102. Dibenz(a,h)anthracene	53-70-3	10	330
103. Benzo(g,h,i)perylene	191-24-2	10	330

[c]Medium Water Contract Required Detection Limits (CRDL) for Semi-Volatile HSL Compounds are 100 times the individual Low Water CRDL.

[d]Medium Soil/Sediment Contract Required Detection Limits (CRDL) for Semi-Volatile HSL Compounds are 60 times the individual Low Soil/Sediment CRDL.

Pesticides	CAS Number	Detection Limits* Low Water[e] ug/L	Low Soil/Sediment[f] ug/Kg
104. alpha-BHC	319-84-6	0.05	8.0
105. beta-BHC	319-85-7	0.05	8.0
106. delta-BHC	319-86-8	0.05	8.0
107. gamma-BHC (Lindane)	58-89-9	0.05	8.0
108. Heptachlor	76-44-8	0.05	8.0
109. Aldrin	309-00-2	0.05	8.0
110. Heptachlor Epoxide	1024-57-3	0.05	8.0
111. Endosulfan I	959-98-8	0.05	8.0
112. Dieldrin	60-57-1	0.10	16.0
113. 4,4'-DDE	72-55-9	0.10	16.0
114. Endrin	72-20-8	0.10	16.0
115. Endosulfen II	33213-65-9	0.10	16.0
116. 4,4'-DDD	72-54-8	0.10	16.0
117. Endrin Aldehyde	7421-93-4	0.10	16.0
118. Endosulfan Sulfate	1031-07-8	0.10	16.0
119. 4,4'-DDT	50-29-3	0.10	16.0
120. Endrin Ketone	53494-70-5	0.10	16.0
121. Methoxychlor	72-43-5	0.5	80.0
122. Chlordane	57-74-9	0.5	80.0
123. Toxephene	8001-35-2	1.0	160.0
124. AROCLOR-1016	12674-11-2	0.5	80.0
125. AROCLOR-1221	11104-28-2	0.5	80.0
126. AROCLOR-1232	11141-16-5	0.5	80.0
127. AROCLOR-1242	53469-21-9	0.5	80.0
128. AROCLOR-1248	12672-29-6	0.5	80.0
129. AROCLOR-1254	11097-69-1	1.0	160.0
130. AROCLOR-1260	11096-82-5	1.0	160.0

[e]Medium Water Contract Required Detection Limits (CRDL) for Pesticide HSL Compounds are 100 times the individual Low Water CRDL.

[f]Medium Soil/Sediment Contract Required Detection Limits (CRDL) for Pesticide HSL compounds are 15 times the individual Low Soil/Sediment CRDL.

*Detection limits listed for soil/sediment are based on wet weight. The detection limits calculated by the labnratory for soil/sediment, calculated on dry weight hasis, as required by the contract, will be higher.

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

EXHIBIT D - ANALYTICAL METHODS

TABLE OF CONTENTS

SECTION 1

INTRODUCTION

The analytical methods that follow are designed to analyze water, sediment and soil from hazardous waste sites for the organic compounds on the Hazardous Substance List (HSL) (See Exhibit C). The methods are based on EPA Methods 608 (Pesticides and PCBs), 624 (Purgeables) and 625 (Base/Neutrals and Acids).

The methods are divided into the following sections: Sample Preparation, Screening, and Analysis. Sample Preparation covers sample extraction and cleanup techniques. As described in the screening section, a portion of the extracts may be screened on a gas chromatograph with appropriate detectors to determine the concentration level of organics. The analysis section contains the GC/MS analytical methods for organics and the gas chromatograph/electron capture detector (GC/ECD) method for pesticides and PCBs. The purge and trap technique, including related sample preparation, is included in the analysis section because GC/MS operation and the purge and trap technique are completely interrelated.

1. Method for the Determination of Purgeable (Volatile) Organic Compounds.

1.1 Scope and Application

This method covers the determination of a number of the HSL purgeable organics as listed in EPA Exhibit C. The method detection limits are also listed in Exhibit C. The method includes an optional hexadecane screening procedure. The extract is screened on a gas chromatograph/flame ionization detector (GC/FID) to determine the approximate concentration of organic constituents in the sample. The actual analysis is based on a purge and trap gas chromatographic/mass spectrometer (GC/MS) method. For sediment/soil samples, the purge device is heated.

2. Method for the Determination of Extractable Base/Neutral and Acid (Semivolatile) Organic Compounds.

2.1 Scope and Application

This method covers the determination of a number of organic compounds that are partioned into an organic solvent and are amenable to gas chromatography. These HSL compounds, and the method detection limits are listed in Exhibit C.

Problems have been associated with the following compounds covered by this method. Benzidine, dichlorobenzidine, aniline, and 4-chloroaniline can be subject to oxidative losses during solvent concentration. This is especially true in the sediment/soil method when concentrating the methylene chloride/acetone extraction solvent. Benzidine can be subject to oxidative losses during solvent concentration. α-BHC, γ-BHC, Endosulfan I and II, and Endrin are subject to decomposition under alkaline conditions. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction

in acetone solution and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet forming diphenylamine and consequently cannot be seperated from diphenylamine native to the sample.

2.2 The method involves solvent extraction of the matrix, and sample characterization to determine appropriate analytical protocol to be used, and GC/MS analysis to determine BNA organic compounds present in the sample.

3. Method for the Determination of Pesticides

3.1 Scope and Application

This method covers the determination of certain HSL organochloride pesticides and polychlorinated biphenyls and the method detection limits are listed in Exhibit C.

3.2 Method Summary

3.2.1 Pesticides and PCBs - The method involves solvent extraction of the matrix, screening of the extract on a gas chromatograph/ electron capture detector (GC/ECD) using a packed column, and quantitation and confirmation on a GC/ECD using a second packed column. (An optional FSCC column may be used for confirmation.) If concentration permits, confirmation is to be done on GC/MS.

SECTION II

SAMPLE PREPARATION AND STORAGE

PART A - SAMPLE STORAGE

1. Procedures for Sample Storage

1.1 The samples must be protected from light and refrigerated at 4°C from the time of receipt until extraction.

1.2 Water samplee muet be extracted within 5 days of receipt and completely analyzed within 40 daye of eatraction. VOA analysie of water samples must be performed within 7 days of sample receipt. Soil samples muet be extracted within 10 days of eample raceipt and completely analyzed within 40 days of extraction. VOA analysis of soil samplee must be performed within 10 days nf aemple raceipt.

NOTE: This does not preclude the contract requirement of 30-day turn-around of analytical data.

PART B - PROTOCOLS FOR WATER

1. Sample Preparation for Pesticides/PCBs

1.1 Summary of Method

A measured volume of sample, approximately one-liter, 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. Optional cleanup techniques are included.

1.2 Interferences

1.2.1 Method interferences may be caused by contaminates 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 phthalates. These phthalates are easily extracted or leached from 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 [4,5].

1.2.2 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 1.8 thru 1.9 must be used to overcome such interferences to attempt to achieve the MDL's.

1.3 Apparatus and Materials

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

1.3.1.1 Separatory funnel - 2000 mL with Teflon stopcock.

1.3.1.2 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.)

1.3.1.3 Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

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

1.3.1.5 Snyder column - Kuderna-Danish, Three-ball macro (Kontes K-503000-0121 or equivalent).

1.3.1.6 Snyder column - Kuderna-Danish, Two-ball micro (Kontes K-569001-0219 or equivalent).

1.3.1.7 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.)

1.3.1.8 Vials - Amber glass, 10 to 15 mL capacity, with Teflon-lined screw cap.

1.3.1.9 Bottle or test tube - 50 mL with Teflon lined screw cap for sulfur removal.

1.3.1.10 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 pipets 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).

1.3.2 Pyrex glass wool - pre-rinse glass wool with appropriate solvents to insure its cleanliness.

1.3.3 Silicon carbide boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

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

1.3.5 Balance - Analytical, capable of accurately weighing 0.0001 gm.

1.3.6 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.

1.4 Reagents

1.4.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the MDL of each parameter of interest.

1.4.2 Acetone, hexane, isooctane (2,2,4-trimethylpentane), methylene chloride - Pesticide quality or equivalent.

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

1.4.4 Alumina - Neutral, Super I Woelm or equivalent. Prepare activity III by adding 7% (w/w) reagent water to the Super I neutral alumina. Tumble or shake in a wrist action shaker for a minimum of 2 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. (Universal Scientific, Incorporated, Atlanta, Georgia or equivalent.) The data must be retained by the laboratory and made available for inspection during on-site evaluations.

1.4.4.1 Alumina Equivalency Check. Test the alumina by adding the BNA surrogates in 1:1 acetone/hexane to the alumina and following paragraph 1.7. 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 $\geq$80%, except for endosulfan sulfate which must be $\geq$60% and endrin ketone which is not recovered.

1.4.5 Sodium hydroxide solution (10N)-(ACS). Dissolve 40g NaOH in reagent water and dilute to 100 mL.

1.4.6 Tetrabutylammonium (TBA) - Sulfite reagent. Dissolve 3.39 g tetrabutylammonium 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.

1.4.7 Pesticide surrogate standard spiking solution.

1.4.7.1 The surrogate standard is added to all samples and calibration solutions; the compound specified for this purpose is dibutyl chlorendate.

1.4.7.2 Prepare a surrogate standard spiking solution at a concentration of 1 ng/1.00 mL in acetone. Addition of 1.00 mL of this solution to 1000-mL of sample is equivalent to a concentration of 1 ug/L of the surrogate standard. Store the spiking solutions at 4°C in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

1.4.8 Sulfuric acid solution (1+1)-(ACS). Slowly, add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

1.4.9 Pesticide matrix standard spiking solution. Prepare a spiking solution of acetone or methanol that contains the following pesticides in the concentrations specified.

Pesticide	ug/1.0 mL
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dialdrin	0.5
Endrin	0.5
4,4' DDT	0.5

Matrix spikes are also to serve as duplicates. Therefore, add 1.0 ml to each of two 1-liter portions from the one sample chosen for spiking.

1.4.10 See Exhibit A for a summary of the quality control requirements of this contract. See Exhibit E for contract-required Quality Control/Quality Assurance procedures.

1.5 Sample Extraction - Separatory Funnel

1.5.1 Samples are usually extracted using separatory funnel techniques. If emulsions will prevent achieving acceptable solvent recovery with separatory funnel extractions, continuous extraction (paragraph 1.6) may be used. The separatory funnel extraction scheme described below assumes a sample volume of one liter.

1.5.2 Using a 1-liter graduated cylinder, measure out a 1-liter sample aliquot and place it into a 2-liter separatory funnel. Pipette 1.0 mL surrogate standard spiking solution into the separatory funnel 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.

NOTE: Recovery of dibutylchlorendate will be low if pH is outside this range.

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 means. Drain methylene chloride into a 250 mL Erlenmeyer flask.

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.

1.5.5 Assemble a Kuderna-Danish (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 listed in Exhibit C.

1.5.6 Pour the combined extract through a drying column containing about 10 cm of anhydrous 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.

1.5.7 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 about 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. 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.

1.5.8 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 about 1 mL of hexane to the top. Concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. 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.

1.5.9 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 1.8; otherwise continue to paragraph 1.5.10.

1.5.10 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 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.

1.5.11 Dilute the extract to 1 mL with acetone and proceed to 1.7 Alumina Column Cleanup.

1.6 Sample Extraction - Continuous Extractor

1.6.1 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 1.5.3 using a seperatory funnel, a continuous extractor should be used.

1.6.2 Using a 1-liter graduated cylinder, measure out a 1-liter sample aliquot and place it into the continuous extractor. Pipette 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.

1.6.3 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 1.5.5 through 1.5.11.

1.7 Alumina Column Cleanup

1.7.1 Add 3 gm of activity III neutral alumina to the 10-mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

1.7.2 Transfer the 1 mL of hexane/acetone extract from paragraph 1.5.11 to the top of the alumina using a disposable Pastaur pipet. Collect the eluate in a clean 10-mL concentrator tube.

1.7.3 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 addition and elution of the sample.

1.7.4 Adjust the extract to a final volume of 10 mL using hexane.

1.7.5 The pesticide/PCB fraction is ready for analysis. Proceed to Section IV, paragraph 3. Store the extracts at 4°C in the dark in Teflon-sealed containers until analyses are performed.

1.8 Sulfur Cleanup

1.8.1 Concentrate the hexane extract from paragraph 1.5.9 to 1 mL.

1.8.2 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.

1.8.3 Add 1 mL TBA-sulfite reagent and 2 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals precipated 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.

1.8.4 Add 5 mL distilled water and shake for at least 1 minute. Allow the sample to stand 5-10 minutes. Transfer the hexane layer (top) to a concentrator ampul and go back to paragraph 1.5.10.

2. Sample Preparation for Extracteble Base/Neuttals and Acids (BNA, Semivolatiles).

2.1 Summary of Method

2.1.1 A measured volume of sample, apptoximately 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.

2.2 Interferences

2.2.1 Method interfereoces 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 ruoning laboratory reagent blanks. Matrix interferences may be caused by contaminents 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 industrial complex or municipality being sampled.

2.3 Apparatus and Materials

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

2.3.1.1 Separatory funnel - 2,000 mL, with teflon stopcock.

2.3.1.2 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.)

2.3.1.3 Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

2.3.1.4 Evaporative flask - Kuderna-Danish, 500 mL (Kontes K-570001 0500 or equivalent). Attach to concentrator tube with springe.

2.3.1.5 Snyder column - Kuderna-Danish, Three-ball macro (Kontes K-503000 0121 or equivalent).

2.3.1.6 Snyder column - Kuderna-Daniab, Two-ball micro (Kontes K569001 D219 or equivalent).

2.3.1.7 Vials - Amber glass, 2 mL capacity with Teflon-lined screw cap.

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

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

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

2.3.4 Balance - Analytical, capable of accurately weighing 0.0001 g.

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

2.4 Reagents

2.4.1 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.

2.4.2 Sodium hydroxide solution (10N) - Dissolve 40g NaOH in reagent water and dilute to 100 mL.

2.4.3 Sodium thiosulfate - (ACS) Granular.

2.4.4 Sulfuric acid solution (1+1) - Slowly add 50 mL of H_2SO_4 (sp gr.1.84) to 50 mL of reagent water.

2.4.5 Acetone, methanol, methylene chloride - Pesticide quality or equivalent.

2.4.6 Sodium sulfate - (ACS) Granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray.

2.4.7 Surrogate standard spiking solution.

2.4.7.1 Surrogate standards are added to all samples and calibration solutions; the compounds specified for this purpose are phenol-d_6; 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.

2.4.7.2 Prepare a surrogate standard spiking solution that contains the base/neutral compounds at a concentration of 100 ug/mL, and the acid compounds at 200 ng/mL. The addition of 1.0 mL of this solution to 1000 mL of sample is equivalent to a concentration of 100 ng/L of each base/neutral surrogate standard and 200 ug/L of each acid surrogate standard. Store the spiking solutions at 4°C in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

2.4.8 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
di-n-butylphthalate	4-chloro-3-methylphenol
pyrene	4-nitrophenol
N-nitroso-di-n-propylamine	
1,4-dichlorobenzene	

Prepare a spiking solution that contains each of the base/neutral compounds above at 100 ug/1.0 mL in methanol and the acid compounds at 200 ug/1.0 ml in methanol. Add 1.0 mL of this to each sample aliquot designated as a BNA matrix spike sample. Analyze duplicate aliquots of a sample spiked with BNA matrix spiking solution.

2.5 Sample Extraction - Separatory Funnel

2.5.1 Samples are usually extracted using separatory funnel techniques. If emulsions will prevent achieving acceptable solvent recovery with separatory funnel extraction, continuous extraction (paragraph 2.6) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1-liter.

2.5.2 Using a 1-liter graduated cylinder, measure out a 1-liter sample aliquot and place it into a 2-liter separatory funnel. Pipet 1.0 mL surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide range pH paper and adjust to pH > 11 with 10N sodium hydroxide.

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 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 2.6.3.

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. Label the combined extract as the base/neutral fraction.

2.5.5 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 2.5.3. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extract as the acid fraction.

2.5.6 Assemble a Kuderna-Danish (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 listed in Exhibit C.

2.5.7 Transfer the individual base/neutral and acid fractions by pouring extracts through separate drying columns containing about 10 cm of anhydrous sodium sulfate, and collect the extracts in the separate K-D concentrators. Rinse the Erlenmeyer flasks and columns with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

2.5.8 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 about 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. 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 at 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.

2.5.9 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 about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a 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. 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 at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and its lower joint into the concentrator tube with 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.

2.5.10 Nitrogen blowdown technique (taken from ASTM Method D3086)

The following method may be used for final concentration, instead of the procedure outlined in paragraph 2.5.9. 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 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.

2.6 Sample Extraction - Continuous Extractor

2.6.1 When experience with a sample for a given source indicates that a serious emulsion problem will result or if an emulsion is encountered in paragraph 2.5.3 using a seperatory funnel, a continuous extractor should be used.

2.6.2 Check the pH of the sample with wide-range pH paper and adjust to pH 11 with 10 N sodium hydroxide. Transfer a 1-liter sample aliquot to the continuous extractor; using a pipet, add 1 mL of surrogate standard spiking solution and mix well.

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 2.5.6 through 2.5.8. Hold the concentrated extract for combining with the acid extract (see paragreph 2.6.4).

2.6.4 Add 500 mL of methylene chloride to a clean distilling flask and attach it to the continous 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 paregraphs 2.5.6 through 2.5.8. Hold the concentrated extract and label as the acid extract.

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

2.7 The samples extracts are ready for GC/MS analysis. Proceed to Section IV, GC/MS Analysis of Extractables. If high concentrations are suspected (e.g. highly colored extracts) the optional GC/FID screen in Section III is recommended.

Section II Part C
Analytical Scheme for Extractable Organics and Pesticide/PCBs in Sediment/Soil

It is mandatory to characterize all soil/sediment samples so that the appropriate analytical protocol may be chosen to ensure proper detection 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 a description of the concentration ranges that are encompassed by the "low" and "medium" level procedures.

The laboratory is at 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" 30g extract or an aliquot from the medium level 1g extract (note: decision on pesticide level will be the same as the BNA)

- Screen using either GC/FID or GC/MS as the screening instrument.

The concentration ranges covered by these two procedures may be considered to be approximately 330 ug/kg - 20,000 ug/kg for the low level analysis and >20,000 ug/kg for medium level analysis for BNA extractables.

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 ug/kg in the original sample, discard the 30 gm extract and follow the medium level methods for organics and pesticides/PCBs using medium level surrogates. If the sample concentration is <20,000 ug/kg, proceed with concentration and the remainder of the low level method.

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 >20,000 ug/kg proceed with GC/MS analysis of the organics and prepare a pesticide/PCB extract by the medium level method. If the sample concentration is <20,000 ug/kg discard the medium level extract and follow the low level method.

1. Medium Level Preparation for Screening and Analysis of Extractable Base/Neutrals and Acids (Semivolatiles, BNA), and Pesticides/PCBs in Sediment Soil

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 ug/kg.

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, pesticide/PCBs, 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.

1.1.2 If the screenings indicate no detectable pollutants at the lower limits of detection, the sample should be prepared by the low level protocol in Section II, Part B.

1.2 Summary of Method

1.2.1 Approximately 1 gram 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.

1.2.2 If organic compounds are detected by the screen, the methylene chloride extract is analyzed by GC/MS for extractable organics. A separate 1 gm sample is also extracted with 10.0 mL of hexane for analysis by GC/EC for Pesticides/PCBs.

1.2.3 If no organic compounds are detected by the medium level screen, then a low level sample preparation is required.

1.3 Interferences

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, depending upon the nature and diversity of the industrial complex or municipality being sampled.

1.4 Limitations

1.4.1 The procedure is designed to allow detection limits for screening purposes as low as 20,000 ug/kg for extractable organics and pesticides/PCBs. For analysis purposes, the detection limits are 20,000 ng/kg for extractable organics and 1,000 ug/kg for pesticide/PCBs. If peaks are present based on the GC/F10 screen, the sample is determined to require a medium level analysis by GC/MS and GC/EC. Some samples may contain high concentrations of chemicals that interfer with the analysis of other components at lower levels; the detection limits in those cases may be significantly higher.

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 detection 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.

1.5 Reagents

1.5.1 Sodium Sulfate - anhydrous and 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.

1.5.2 Methylene chloride. Pesticide residue analysis grade or equivalent.

1.5.3 Hexane. Pesticide residue analysis grade or equivalent.

1.5.4 Methanol. Pesticide residue analysis grade or equivalent.

1.5.5 Acetone. Pesticide residue analysis grade or equivalent.

1.5.6 Base/Neutral and Acid Surrogate Standard Spiking Solution

1.5.6.1 The compounds specified are phenol-d6, 2,4,6-tribromophenol, 2-fluorophenol, nitrobenzene-d_5, terpheoyl-d_{14} and 2-fluorobiphenyl. Prepare a solution containing these compounds for base/neutral surrogates at a concentration of 100 ug/1.0 mL, and for acid surrogate standards at a concentration of 200 ug/1.0mL in methanol.

1.5.7 Pesticide/PCB Surrogate Standard Spiking solution.

1.5.7.1 The compound specified is dibutyl chlorendate. Prepare a solution at a concentration of 20 ug/1.0 mL in methanol.

1.5.8 Base/Neutral and Acid Matrix Standard Spiking solution.

1.5.8.1 Prepare a spiking solution in methanol that contains the following compounds at a concentration of 100 ug/1.0 mL for base/neutrals and 200 ug/1.0 mL for acids:

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

1.5.9 Pesticide/PCB Matrix Standard Spiking solution

1.5.9.1 Prepare a spiking solution in methanol that contains the following pesticides in the concentrations specified.

Pesticide	ug/1.0mL
lindane	2.0
heptachlor	2.0
aldrin	2.0
dieldrin	5.0
endrin	5.0
4,4' DDT	5.0

1.5.10 Alumina - neutral, super 1 Woelm or equivalent (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 2 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.

1.5.11 Alumina Equivelency Check. Test the alumina by adding the BNA surrogates in 1:1 acetone/hexane to the alumina and following paragraph 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 compooent pesticides must be $\geq$80%, except for sodosulfan sulfate which must be $\geq$60% and adrin ketone which is not recovered. The data must be retained by the laboratory and made available for inspection during on-site evaluations.

1.6 Equipment

1.6.1 Glass scintillation vials, at least 20 mL, with screw cap and teflon or aluminum foil liner.

1.6.2 Spatula. Stainless steel or Teflon (R).

1.6.3 Balance capable of weighing 100 grams to the nearest 0.01 gram.

1.6.4 Vials and caps, 2 mL for GC auto sampler.

1.6.5 Disposable pipets, Pasteur; glass wool rinsed with methylene chloride.

1.6.6 15-mL concentrator tubes.

1.6.7 Sonic cell diruptor, heat systems - Ultrasonics, Inc., Model 357C or equivalent (375 watt with pulsing capability and microtip).

1.6.8 Sonabox - recommended with above disruptors for decreasing cavitation sound.

1.6.9 Test tube rack.

1.6.10 Oven, drying

1.6.11 Desiccator

1.6.12 Crucibles, porcelain

1.6.13 Chromatography column for alumina. 8 mL (200 mm & 8 mm ID) Polypropylene column (Kontes K-420160 or equivelent) or 6 mL (150 mm X 8 mm ID) glass column (Kontes K-420155 or equivalent) or 5 mL serological pipets 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).

1.7 Sample Preparation

1.7.1 Medium level preparation for screening and analysis for extractable organics.

1.7.1.1 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 gram (record weight to the 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 sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

1.7.1.2 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.

$$\frac{\text{gm of sample} - \text{gm of dry sample}}{\text{gm of sample}} \times 100 = \text{X moisture}$$

1.7.1.3 Add 2.0 gm of anhydrous sodium sulfate to sample in the 20 mL vial from paragraph 1.7.1.1 and mix well.

1.7.1.4 Surrogate Standards are added to all samples, spikes, and blanks. Add 1.0 mL of surrogate spiking solution to sample mixture.

1.7.1.5 Add 1.0 mL of matrix standard spiking solution to each of two 1-gram portions from the sample chosen for spiking.

1.7.1.6 Immediately add 9.0 mL of methylene chloride to the sample and disrupt the sample by ultrasonic probe for 2 minutes at 100 watts power.

1.7.1.6.1 Add only 8.0 mL of methylene chloride to the matrix spike samples to achieve a final volume of 10 mL.

1.7.1.7 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.

1.7.1.8 Concentrate the extract to 1.0 mL by the nitrogen blowdown technique described in Section II, Part C, paragraph 2.7.3.

1.7.1.9 Transfer the concentrate to an autosampler viel for GC/FID or GC/MS capillary column screening. If the concentrate is screened, the detection limits should be approximately 20,000 ug/kg.

1.7.1.10 Proceed to Section III, paragraph 2.0.

1.7.2 Medium Level prep for analysis of Pesticide/PCBs (Determine results of GC/FID screen before proceeding.

1.7.2.1 Transfer the sample container into a fume hood. Open the sample vial and mix the sample. Transfer approximately 1 gram (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.

1.7.2.1.1 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. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less then 5, contact the Project Officer or Deputy Project Officer 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.

1.7.2.2 Add 2 gm of anhydrous sodium sulfate to the sample and mix well.

1.7.2.3 Surrogate standards are added to all samples, spikes, and blanks. Add 50 nL of surrogate spiking solution to the sample mixture.

1.7.2.4 Add 1.0 mL of matrix standard spiking solution to each of two 1-gram portions from the sample chosen for spiking.

1.7.2.5 Immediately add 10.0 mL (only 9.0 mL for the matrix spike sample) of hexane to the sample and disrupt the sample by ultrasonic probe for 2 minutes at 100 watts with pulse set at 50 percent.

1.7.2.6 Loosely pack disposable Pasteur pipets with 2-3 cm glass wool plugs. Filter the extract through the glass wool and collect at approximately 5 mL in a concentrator tube.

1.7.2.7 Transfer 1.0 mL of the hexane extract to a glass concentrator tube and concentrate to 0.5 mL using Nitrogen blowdown. 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.

1.7.2.8 Follow the procedures for low level soil sediment preparation outlined in paragraphs 2.8.1.1 through 2.8.3.3 for alumina cleanup and sulfur removal.

2. Low Level Preparation for Screening and Analysis of Extractable Base/Neutrals and Acids (Semivolatiles BNA), and Pesticides/ PCBs (PEST) in Sediment/Soil.

2.1 Summary of Method

2.1.1 A 30 gram portion of sediment is mixed with anhydrous 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 ug/kg, discard the extract and prepare the sample by the medium level method. If no peaks are present at greater than 20,000 ug/kg, the extract is concentrated and split into two fractions. An optional gel permeation column cleanup may be used before splitting the extract. One fraction is for GC/MS analysis of BNA. The other fraction is cleaned up using a micro alumina column and analyzed by GC/EC for pesticides.

2.2 Interferences

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, depending upon the nature and diversity of the industrial complex or municipality being sampled.

2.3 Apparatus and Materials

2.3.1 Apparatus for determining percent moisture

2.3.1.1 Oven, drying

2.3.1.2 Desiccator

2.3.1.3 Crucibles, porcelain

2.3.2 Disposable Pasteur glass pipets, 1 mL

2.3.3 Sonic cell disruptor, Heat Systems - Ultrasonics, Inc. Model 375C or equivalent (375 watt with pulsing capability and 3/4" disruptor horn).

2.3.4 Beakers, 400 mL

2.3.5 Vacuum filtration apparatus

2.3.5.1 Buchner funnel.

2.3.5.2 Filter paper, Whatman No. 41 or equivalent.

2.3.6 Kuderna-Danish (K-D) apparatus.

2.3.6.1 Concentrator tube - 10 mL, graduated (Kontes K-570040-1029 or equivalent).

2.3.6.2 Evaporative flask - 500 mL (Kontes K-570001-0500 or equivalent).

2.3.6.3 Snyder column - three-ball macro (Kontes K-503000-0121 or equivalent).

2.3.6.4 Snyder column - two ball micro (Kontes K-569001-0219) or equivalent).

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

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

2.3.9 Top loading balance, capable of accuretely weighing 0.01 gm.

2.3.10 Vials and caps, 2 mL for GC auto sampler.

2.3.11 Balance - Analytical, capable of accurately weighing 0.0001 gm.

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.

2.3.13 Gel permeation chromatography cleanup device.

2.3.13.1 Automated system

2.3.13.1.1 Gel permeation chromatograph (GPC) Analytical Biochemical Labs, Inc. GPC Autoprep 1002 or equivalent including:

2.3.13.1.2 25 mm ID X 600 - 700 mm glass column packed with 70 gm of Bio-Beeds SX-3.

2.3.13.1.3 Syringe, 10 mL with luer lok fitting.

2.3.13.1.4 Syringe filter holder and filters - stainless steel and TFE, Gelman 4310 or equivalent.

2.3.13.2 Manual system assembled from parts.*

2.3.13.2.1 25 mm ID X 600 - 700 mm heavy wall glass column packed with 70 gm of BIO-Beads SX-3.

2.3.13.2.2 Pump: Altex Scientific, Model No. 1001A, semipreparative, solvent metering system. Pump capacity - 28 mL/min.

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

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

2.3.13.2.5 Injector: Altex Scientific, catalog No. 201-56, sample injection valve, Tefael, with 10 mL sample loop.

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

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

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*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

2.3.13.2.8 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.

2.3.14 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 pipets 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).

2.3.15 Pyrex glass wool.

2.3.16 Bottle or test tube, 50 mL with Teflon lined screw cap for sulfur removal.

2.3.17 Pasteur pipets, disposable.

2.4 Reagents

2.4.1 Sodium Sulfate - anhydrous and 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.

2.4.2 Methylene chloride, hexane, acetone, isooctane, 2 propanol and benzene pesticide quality or equivalent.

2.4.3 Alumina - neutral, super I Woelm or equivalent (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 2 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. See page D-28, paragraph 1.5.11.

2.4.4 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.

2.4.5 Tetrabutylammonium (TBA) - sulfite reagent. Dissolve 3.39 g tetrabutylammonium 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.

2.4.6 GPC calibration solutions:

2.4.6.1 Corn oil - 200 mg/mL in methylene chloride.

2.4.6.2 Bis(2-ethylhexyl)phthalate) and pentachlorophenol - 4.0 mg/mL in methylene chloride.

2.4.7 Sodium Sulfite, reagent grade.

2.4.8 Surrogate standard spiking solution.

2.4.8.1 Base/neutral and acid surrogate solution.

2.4.8.1.1 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_6, 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.

2.4.8.1.2 Prepare a surrogate standard spiking solution at a concentration of 100 ug/1.0 mL for BN and 200 ug/1.0 mL for acids in methanol. Addition of 0.5 mL of this solution to 30 gm of sample is equivalent to a concentration of 1700 ug/kg for base/neutrals and 3,330 ug/kg for acids of each surrogate standard. Store the spiking solutions at 4°C in Teflon-sealed containers. The solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

2.4.8.2 Pesticide surrogate standard spiking solution.

2.4.8.2.1 The surrogate standard is added to all samples, blanks, matrix spike, matrix spike duplicates, and calibrations solutions; the compound specified for this purpose is dibutyl chlorendate.

2.4.8.2.2 Prepare a surrogate standard spiking solution at a concentration of 20 ug/1.0 mL in methanol.

Addition of 100 uL of this solution to 30 gm of sample is equivalent to a concentration of 67 ug/kg of surrogate standard. Store the spiking solutions at 4°C in Teflon-sealed containers. The solutions should be checked frequently for stability. These solntions must be replaced after six months, or sooner if comparison with qnality contrnl check samples indicace a problem.

2.4.9 Matrix standard spiking solutions.

2.4.9.1 Base/neutral and acid matrix spiking solution consists of:

Base/Neutrals (100 ug/1.0 mL)	Acids (200 ug/1.0 mL)
1,2,4-trichlorobenzene	pentachlorophenol
acenaphthene	phenol
2,4-dinitrotoluene	2-chlorophenol
di-n-butylphthalate	4-chloro-3-methylphenol
pyrene	4-nitrophenol
N-nitroso-di-n-propylamine	
1,4-dichlorobenzene	

Prepare a spiking solution that contains each of the above in methanol.

Matrix spikes also serve as duplicates, therefore, add 0.5 mL to each of two 30 gm portions from one sample chosen for spiking.

2.4.9.2 Pesticide matrix standard spiking solution. Prepare a spiking solution in methanol that contains the following pesticides in the concentrations specified.

Pesticide	ug/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 400 uL to each of two 30 gm portions from one sample chosen for spiking.

2.5 Sample Extraction

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.

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 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 Project Officer or Deputy Project Officer 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.

2.5.2 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 gms of sample to the nearest 0.1 gram into a 400-mL beaker and add 60 gms of anhydrous 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.

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.

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

2.5.2.2 Weigh out four 30 gm (record weight to nearest 0.1g) portions for use as matrix and matrix spike duplicates and as matrix spikes. Follow 2.5.2 and then add 1.0 mL of the base/neutral and acid matrix spike to each of two portions and 400 uL of the pesticide matrix spike to each of the other two portions.

2.5.2.3 Add 1.0 mL of base/neutral and acid surrogate standard and 100 uL of pesticide surrogate to the sample.

2.5.3 Place the probe about 1/2" below the surface of the solvent but above the sediment layer.

2.5.4 Sonicate for 3 min., using 3/4" horn, at full power with pulse set at 50%. Do not use microtip.

2.5.5 Decant and filter extracts through Whatman #41 filter peper using vacuum filtration or centrifuge and decant extraction solvent.

2.5.6 Repeat the extraction two more times with 2 additional 100 mL portions of 1:1 methylene chloride - acetone. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 methylene chloride - acetone.

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 2.7.2 or 2.7.3. Note that the sample volume in this case is 5.0 mL not 8.0 mL as given in 2.7.2. Screen the extract as per Section III, paragraph 2, "Screening of Extractable Organic Extracts". Transfer the remainder of the 1 mL back to the total extract from paragraph 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.)

2.5.7 Transfer the extract to a Kuderna-Danish (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 Exhibit C.

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 about 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. 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 10mL volume with methylene chloride.

2.5.9 If GPC cleanup is not used proceed to paragraph 2.7.

2.6. Extract Cleanup

2.6.1 GPC Setup and Calibration

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.

2.6.1.2 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 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 point. Choose a "dump time" which allows $\geq$ 85% removal of the corn oil and $\geq$ 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 nm 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.

2.6.2 GPC Extract Cleanup

Prefilter or load all extracts via the filter holder to avoid particulates that might cause flow stoppage. Load one 5.0 mL aliquot of the extract onto the GPC column. Do not apply

Table 7.

Chromatographic Conditions for Pesticides/PCBs*

Parameter	Typical Retention Time (min) Column 1*	Column 2
alpha-BHC	1.45	1.64
gamma-BHC	1.86	1.94
beta-BHC	2.18	1.76
Heptachlor	2.27	3.21
delta-BHC	2.55	2.01
Aldrin	2.76	4.01
Heptachlor epoxide	4.31	4.98
Endosulfan I	5.46	6.26
4,4'-DDE	6.37	7.51
Dieldrin	6.74	7.38
Endrin	8.25	8.35
4,4'-DDD	10.08	9.53
Endosulfan II	10.14	8.35
4,4'-DDT	12.06	12.75
Endrin aldehyde	13.64	9.53
Endosulfen sulfate	16.73	11.09
Endrin ketone	22.70	-
gamma Chlordane	4.77	5.74
alpha Chlordane	5.24	6.39
Toxaphene	mr	mr
Aroclor-1016	mr	mr
Aroclor-1221	mr	mr
Aroclor-1232	mr	mr
Aroclor-1242	mr	mr
Aroclor-1248	mr	mr
Aroclor-1254	mr	mr
Aroclor-1260	mr	mr
methoxychlor	24.07	19.60
dibutyl chlorendate	21.80	27.21

Column 1 conditions: Gas Chrom Q (80/100 mesh) or equivalent coatad with 1.5% OV-17/1.95% OV-210 or aquivalent 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. (RP 5880) Column temperature, isothermal et 192°C.

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/miu makeup gas). (Tracor 222). Column temperature, isothermal at 194°C.

Capillary column conditions: 30 m x 0.25 mm ID, 0.25 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: oone
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

*GC conditions for attached chromatograms (not contract requirements)

NOTE: 2mm ID column with 80/100 mesh does oot adequately resolve dihutyl chloreodate and endrin ketone.

2.7 Splitting of Extract and Final Concentration

NOTE: If only pesticide or BNA analysis is to be performed on a sample only the appropriate surrogates for that fraction should be added as per paragraph 2.5.2.3 (and only appropriate matrix spikes for duplicate matrix spike samples). The 10 mL extract resulting from paragraph 2.5.8 should not be split as described in paragraph 2.7.1, following, but should be concentrated as follows: to 1.0 mL for BNAs (not to 0.8 mL as in paragraph 2.7.2). However, for pesticides/PCBs, follow 2.7.1 as written, because of the limited cleanup capacity of the micro alumina column.

The alumina clean-up for pesticides is still required when BNA surrogates are not present in order to remove polar interferents.

2.7.1 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. 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 in

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):
- o 1/20 total extract taken for pesticide analysis (derived from 0.5 mL of 10 mL extract)
- o 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. C.)

W_s = Weight of sample extracted (gm)

3.8.2 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.

3.8.3 Calculation for surrogate and matrix spikes recovery.

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

Where: Q_d = quantity determined by analysis
Q_a = quantity added to sample.

Be sure all dilutions are taken into account. Sediment/soil has a 20 time dilution factor built into the method when accounting for one-twentieth of extract taken for pesticide analysis and final dilution to 1 mL.

3.8.4 Report results in micrograms per liter or micrograms per kilogram without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

internal wall of the tube must be rinsed down several times with methylene chloride (hexane for pesticides analysis) during the operation, and the final volume brought to 0.8 mL with methylene chloride (hexane for pesticide analysis). 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 was used, this 0.8 mL represents a 2 times dilution to account for only half the extract going through the GPC.

2.7.4 Store all extracts at 4°C in the dark in Teflon-sealed containers until all analyses are performed.

2.8 Pesticide/PCB.

2.8.1 Alumina Column Cleanup

All samples must be taken through this cleanup technique to eliminate BNA surrogates that will interfere in the GC/ECD analysis.

2.8.1.1 Add 3 gm of activity III neutral alumina to the 10 mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

2.8.1.2 Transfer the 1.0 mL of hexane/acetone extract from paragraph 2.7.1 to the top of the alumina using a disposable Pasteur pipet. Collect the eluate in a clean, 10 mL concentrator tube.

2.8.1.3 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 addition and elution of the sample.

3.7.4.2 Quantitation must be on the packed column chromatogram (primary or confirmation) that provides the best separation from interfering peaks.

3.7.4.2.1 Quantitation of technical chlordane. Weathering and/or different formulations of chlor daoe may modify the technical chlordane pattern shown in Figure 3. If the chlordane pattern in a aample is similar to Figure 3, use a technical chiordane standard for quantitation. If the pattern is differant but gamma and alpha chlordane are present, use gamma and alpha chlordane standards for calculation, total the results, report under technical chlordane but footnote the dara as calculated using gamma and alphe chlordane.

3.7.4.3 Computer reproductions of chromatograms manipulated to ansure all peaks are on scale nver a 100 fold renge is acceptable. However, thia can be no greater than a 100 fold range. This is to prevent retention time shifts by column or derector overload. Also, peak response must be >25% of full acale deflectinn to allow visual pattarn recognirion of multicomponent compounds and individual compounds must be visible.

3.7.4.4 If identification of compounds of interest are prevented by the presence of interferences, further cleanup is required. If aulfur is evident go to "Sulfur Cleaoup" in Section II, B, Sample Preparatiou for Pesticides/PCBs.

2.8.3.3 Add 5 mL distilled water and shake for at least 1 min. Allow the sample to stand for 5-10 min. and remove the hexane layer (top) for analysis. Concentrate the hexane to 1.0 mL as per paragraphs 2.7.1 and 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 column technique. Continue as outlined in paragraph 2.8.2.2.

If none of the DDT series is to be quantitated and DDT exceeds the 10% RSD, simply record the % RSD on the proper form. Any time toxaphene is to be quantitated, follow 3.7.3.1.1.

3.7.3.2 After the linearity standards required in 3.7.3.1 are injected, continue the confirmation analysis injection sequence with all compounds tentatively identified in 3.6, to establish the daily retention time windows. (See paragraph 3.6.1.1.) Analyze all confirmation standards for a case at the beginning, at intervals specified in 3.7.3.3, 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 following the standard that exceeds the criteria.

3.7.3.3 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 each 10 samples). The alternating standard's ratios of the response to the amount injected must be within 15% of each other if quantitation is performed. Deviations larger than 15% require the laboratory to repeat the samples analyzed following the standard that exceeds the criteria. The 15% criteria only pertains to compounds being quantitated.

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.

3. Interferences

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 as described in paragraph 8.5. 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 industrial complex or municipality being sampled.

4. Apparatus and Materials

4.1 Vials and caps, 2 mL for GC auto sampler.

4.2 Volumetric flask, 50 mL with ground glass stopper.

4.3 Pasteur pipets, disposable.

4.4 Centrifuge tube, 50 mL with ground glass stopper or Teflon-lined screw cap.

4.5 Balance - Analytical, capable of accurately weighing 0.0001 gm.

5. Reagents

5.1 Hexadecane and methanol-pesticide residue analysis grade or equivalent.

5.2 Reagent water - Reagent water is defined as water in which an interferant is not observed at the MDL of each parameter of interest.

5.3 Standard mixture #1 containing benzene, toluene, ethyl benzene and xylene. Standard mixture #2 containing n-nonane and n-dodecane.

3.7.2 Table 7 provides examples of operating conditions for the gas chromatograph. Separation should be ≥ 25% resolution between peaks. This criteria must be considered when determining whether to quantitate on the Primary Analysis or the Confirmation Analysis. When this criteria cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

All QC specified in Exhibit E must be adhered to, i.e., the ≥ 12 min. 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.

3.7.3 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. One 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. The detector attenuation must provide peak response equivalent to the Primary Analysis response for each compound to be confirmed.

3.7.3.1 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.

3.7.3.1.1 Toxaphene only - Begin the sequence with Evaluation Mix B to check degredation, followed by three concentration levels of toxaphene. Check linearity by calculating % RSD. If ≤ 10% RSD, use the appropriate equation in paragraph 3.8 for calculation.

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

- o pulling the emulsion through a small plug of Pyrex glass wool packed in a pipet, or
- o transferring the emulsion to a centrifuge tube and centrifuging for several minutes.

6.1.3 Add 200 uL of working standard mixture #1 and #2 to separate 40 mL portions of reagent water. Follow steps 6.1.1 - 6.1.2 beginning with the immediate addition of 2.0 mL of hexadecane.

6.2 Sediment/Soil

6.2.1 Add approximately 10 grams of soil (wet weight) to 40 mL of reagent water in a 50 mL centrifuge tube with a ground glass stopper or teflon-lined cap. Cap and shake vigorously for one minute. Centrifuge the capped flask briefly. Quickly transfer supernatent water to a 50 mL volumetric flask equipped with a ground glass stopper.

6.2.2 Follow 6.1.1, starting with the addition of 2.0 mL of hexadecane.

7. Sample Analysis

The sample is ready for GC/FID Screening. Proceed to Section III, SCREENING, paragraph 1, screening of Hexadecane Extracts for Purgeables.

3.6.3.2 Tentative identification is when the unknown's retention time matches the retention time of a corresponding standard that was chromatographed within a 24 hour period.

3.6.3.3 Determine if any pesticides/PCBs listed in Table 7 are present. The PCB chromatograms in Figure 6-12 should be helpful for pattern recognition.

3.6.3.3.1 If the response for any of these compounds is 100% or less of full scale, the extract is ready for confirmation and quantitation.

3.6.3.3.2 If the response for any compound is greater than 100% of 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.

3.6.3.3.3 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.

3.6.3.3.4 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.

1. Screening of Hexadecane Extracts for Purgeables

1.1 Summary of Method

1.1.1 The hexadecane extracts of water and sediment/soil 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.

1.2 Apparatus and Materials

1.2.1 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.

1.2.1.1 Above GC equipped with flame ionization detector.

1.2.1.2 GC column - 3 m x 2 mm ID glass column packed with 10% OV-101 on 100-120 mesh Chromosorb W-SP (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.

1.3 Reagents

Hexadecane - pesticide residue analysis grade or equivalent.

1.4 Limitations

1.4.1 The flame ionization detector varies considerably in sensitivity when comparing aromatics and halogenated methanes and ethenes. Halomethanes are approximately 20 X less sensitive

IV.

24-Hour Sequence for Pesticide/PCB Analysis:

Sample or Standard

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. Tech. chlordane
8. Aroclors 1016/1260
9. Aroclor 1221
10. Aroclor 1232
11. Aroclor 1242
12. Aroclor 1248
13. Aroclor 1254
14. 5 samples
15. Evaluation standard mix B
16. 5 samples
17. Individual standard mix A or B
18. 5 samples
19. Repeat the above sequence starting with Evaluation Standard Mix B (step 15 above).
20. Pesticide/PCB analysis sequence must end with Individual Standard mix A or B regardless of number of samples analyzed.

* These may be one mixture (see paragraph 3.4.3).

1.5.2 Inject the same volume of hexadecane extract as the extracted standard mixture in 1.5.1. Use the GC conditions specified in 1.2.1.2.

1.6 Analytical Decision Point

1.6.1 Water

1.6.1.1 Compare the hexadecane sample extract chromatograms against the reagent blank and extracted standard chromatograms.

1.6.1.1.1 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.

1.6.1.1.2 If peaks are present prior to the n-dodecane and the aromatics are distinguishable, follow Option A (1.4.2.1).

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

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

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

3.6.1.1 Inject Individual Standard mix A or B and all multi-response pesticides/PCBs at the beginning of each 24 hour sequence. (See paragraph 3.6.2.2.2.) To establish the daily RT window for the pesticides/PCBs 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 or B is analyzed at the beginning, at 12-hour intervals throughout the analysis, and at the end. Any pesticide outside of its established time window requires immediate investigation and correction before continuing the analysis. The laboratory must reanalyze all affected samples.

3.6.1.2 Sample analysis of extracts from Section II, SAMPLE PREPARATION, can begin when linearity and degradation QA/QC criteria specified in Exhibit E have been met. Analyze groups of 5 samples. Evaluation mix B or the Individual Standard mix A or B must be alternately reanalyzed after each group. If a multi-response pesticide/PCB is detected in either of the preceding groups of 5 samples, the appropriate multi-response pesticide/PCB may be substituted for Individual mix A or B. The alternating standard's ratios of the response to the amount injected must be within 15% of each other (20% for confirmation runs). Deviations larger than 15% require the laboratory to repeat the samples analyzed in between. The 15% criteria pertains only to compounds being quantitated. Samples must also be repeated if the degradation of DDT and/or endrin exceeds 20% respectively on the daily intermittant analysis of Evaluation standard mix B.

1.6.3 Sample Analysis

Proceed to Section IV ANALYSES, paragraph 1. "GC/MS Analysis-of Purgeables.

2. Screening of Extractable (Semivolatile) Organic Extracts

2.1 Summary of Method

2.1.1 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.

2.2 Apparatus and Materials

2.2.1 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.

2.2.1.1 Above GC equipped with flame ionization detector.

2.2.1.2 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).

2.3 Reagents

2.3.1 Methylene chloride - pesticide residue analysis grade or equivalent.

3.5 Calibration

3.5.1 The gas chromatographic system must be calibrated using the external stanard technique for all packed columns used for quantitation.

3.5.2 External standard calibration procedure:

3.5.2.1 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 MDL 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.

3.5.2.2 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.

2.3.2.2 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 2.3.2.1.2.

2.4 GC Calibration

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

2.4.1.1 Standardized for 50% full scale response from 50 ng of phenanthrene.

2.4.1.2 Adequately separates phenol from the solvent front.

2.4.1.3 Minimum of 25% full scale response for 50 ng of di-n-octylphthelate.

2.5 GC/FID Screening

2.5.1 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/sec

2.5.2 Inject the GC calibration standard and ensure the criteria specified in 2.4 are met before injecting samples. Estimate the response for 10 ng of phenanthrene.

NOTE: The 2mm ID column cited on page D-124 as Column 1 will not adequately separate dibutyl chlorendate and endrin.

3.3.1.1.2 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.

3.3.1.2 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 equivalent).

3.3.2 Balance-analytical capable of accurately weighing 0.0001 g.

3.4 Reagents

3.4.1 Isooctane (2,2,4-trimethylpentane), hexane, and toluene - Pesticide quality or equivalent.

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

3.4.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams 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.

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

2.6.2.2.3 A separate medium level extract is prepared for Pesticide/PCBs as described in Section II C, paragraph 1.7.2.

2.6.2.3 Peaks are detected at greater than 100% full scale deflection:

2.6.2.3.1 If the screen is from the medium level preperation, calculate the dilution necessary to reduce the major peaks to between 50% and 100% full scale deflection. Use this dilution factor to dilute the extract. This dilution is analyzed by GC/MS for extractable organics.

2.6.2.3.2 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.

2.7 GC/MS Analysis

2.7.1 Use the information from 2.6 to perform the GC/MS analysis of extractables in Section IV, ANALYSIS, paragraph 2.

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 (Lindene)	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
Endrin Aldehyde	67	345, 250
Endosulfan Sulfate	272	387, 422
4,4'-DDT	235	237, 165
Methoxychlor	227	228
Chlordane	373	375, 377
Toxaphene	159	231, 233
Arochlor-1016	222	260, 292
Arochlor-1221	190	222, 260
Arochlor-1232	190	222, 260
Arochlor-1242	222	256, 292
Arnchlor-1248	292	362, 326
Arochlor-1254	292	362, 326
Arochlor-1260	360	362, 394
Endrin Ketone	317	67, 319

Table 6.
Characteristic Ions for Surrogates and
Internal Stendards for Semivolatile Compounds

SURROGATES	Primary Ion	Secondary Ion(s)
Phenol-5	99	42, 71
2-Fluoropheool	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_8	164	162, 160
Phenanthrene-d_8	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265

1. GC/MS Analysis of Purgeable Organics

1.1 Summary of Methods

1.1.1 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.

1.1.2 Sediment/Soil Samples

1.1.2.1 Low Level. An inert gas is bubbled through a mixture of a 5 gm sample and reagent water contained in a suggested specially designed purging chamber (illustrated on page D-95) 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.

Table 4.
Characteristic Ions for Semivolatile HSL Compounds

Parameter	Primary Ion	Secondary Ion(s)
N-Nitrosodimethylamine	42	74, 44
Phenol	94	65, 66
Aniline	93	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	122	107, 121
Benzoic Acid	122	105, 77
bis(-2-Chloroethoxy)Methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobanzane	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
2-Nitroaniline	65	92, 138
Dimetnyl 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	139	109, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	89	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
4-Chlorophanyl-phenylether	204	206, 141

(continued)

1.2.3 Contamination by carry over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry over, 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.

1.3 Apparatus and Materials

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

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

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

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

1.3.5 Glassware

1.3.5.1
- Bottle - 15 mL, screw cap, with Teflon cap liner.
- Volumetric flasks - class A with ground-glass stoppers.
- Vials - 2 mL for GC autosampler.

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.)

Sediment/soil

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

(Dry weight basis)

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 8 mL extract to 0.8 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)

1.3.6.4 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.

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

1.3.7 GC/MS system

1.3.7.1 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.

1.3.7.2 Column - 6 ft long x 0.1 in ID glass, packed with 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent.

1.3.7.3 Mass spectrometer - Capable of scanning from 35 to 260 amu every seven 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.

1.3.7.4 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.

2.6.2.1 Up to 20 substances 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 EPA/NIH 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. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

2.6.2.2 Guidelines for making tentative identification:

(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.

(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.

(3) Molecular ions present in reference spectrum should be present in sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(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. Data system library reduction programs can sometimes create these discrepancies.

1.4.3 Methanol - Pesticide quality or equivalent.

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

1.4.4.1 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.

1.4.4.2 Add the assayed reference material as described below.

1.4.4.2.1 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.

1.4.4.2.2 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.

Initial Column Temperature Hold	- 30°C for 4 minutes
Column Temperature Program	- 30-300°C at 8 degrees/min.
Final Column Temperature Hold	- 300°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/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 any compound saturates the detector, the extract must be diluted and reanalyzed. See "Sample Analysis" in Exhibit E.

2.6 Qualitative Analysis

2.6.1 The target compounds listed in the Hazardous Substances List (HSL), Exhibit C, shall be identified 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.

2.6.1.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within $\pm$ 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. The RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

1.4.7 Purgeable Organic Matrix Standard Spiking Solution

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

Purgeable Organics

1,1-dichloroethene
trichloroethene
chlorobenzene
toluene
benzene

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

1.4.8 BFB Standard - Prepare a 25 ng/uL solotion of BFB in methanol.

1.4.9 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standard solotions be stored at -10°C to -20°C in screw cap amber bottles with teflon liners.

1.5 Calibration

1.5.1 Assemble a purge and trap device that meets the specification in paragraph 1.3.6. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, daily condition traps 10 minutes while back-flushing at 180°C with the column at 220°C.

1.5.2 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 1.7.1.2 Calibrate the purge and trap-GC/MS system using the internal standard technique (paragraph 1.5.3).

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).

2.4.4.1 The average response factor (RF) should 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 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.

2.4.4.2 A % Relative Standard Deviation (%RSD) is calculated for thirteen compounds labeled the Calibration Check Compounds (CCC). A maximum % RSD is also specified for these compounds. These criteria must be met for the calibration curve to be valid.

2.4.5 Check of the calibration curve must be performed once every 12 hours during analysis. These criteria are described in detailed in the instructions for Form VII, Calibration Check. The minimum response factor for the system performance check compounds must be checked. If this criteria is met, the response factor of all compounds is calculated. A percent difference of the daily response factor (12 hour) compared to the average 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.

2.4.6 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

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.

1.5.3.4 The average response factor (RF) 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 response factor. These compounds (the SPCC) are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. Five compounds (the calibration check compounds, CCC) are used to evaluate the curve. Calculate the % Relative Standard Deviation (%RSD) of RF 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.

1.5.3.5 Check of the calibration curve should be performed once every 12 hours. These criteria are described in detail in the instructions for Form VII, Continuing Calibration Check. The minimum response factor for the system performance check compounds must be checked. If this criteria is met, the response factor of all

2.2.1.4 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.

2.3 Reagents

2.3.1 Internal standards - 1,4 dichlorobenzene-d_4, napthalene-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.

2.3.2 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.

2.4 Calibration

2.4.1 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standard solutions be stored at 4°C or less in screw cap amber bottles

1.7 Sample Analysis

1.7.1 Water Samples

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

1.7.1.2 Recommended operating conditions for the gas chromatograph - 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 mL/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.

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

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

1.7.1.5 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

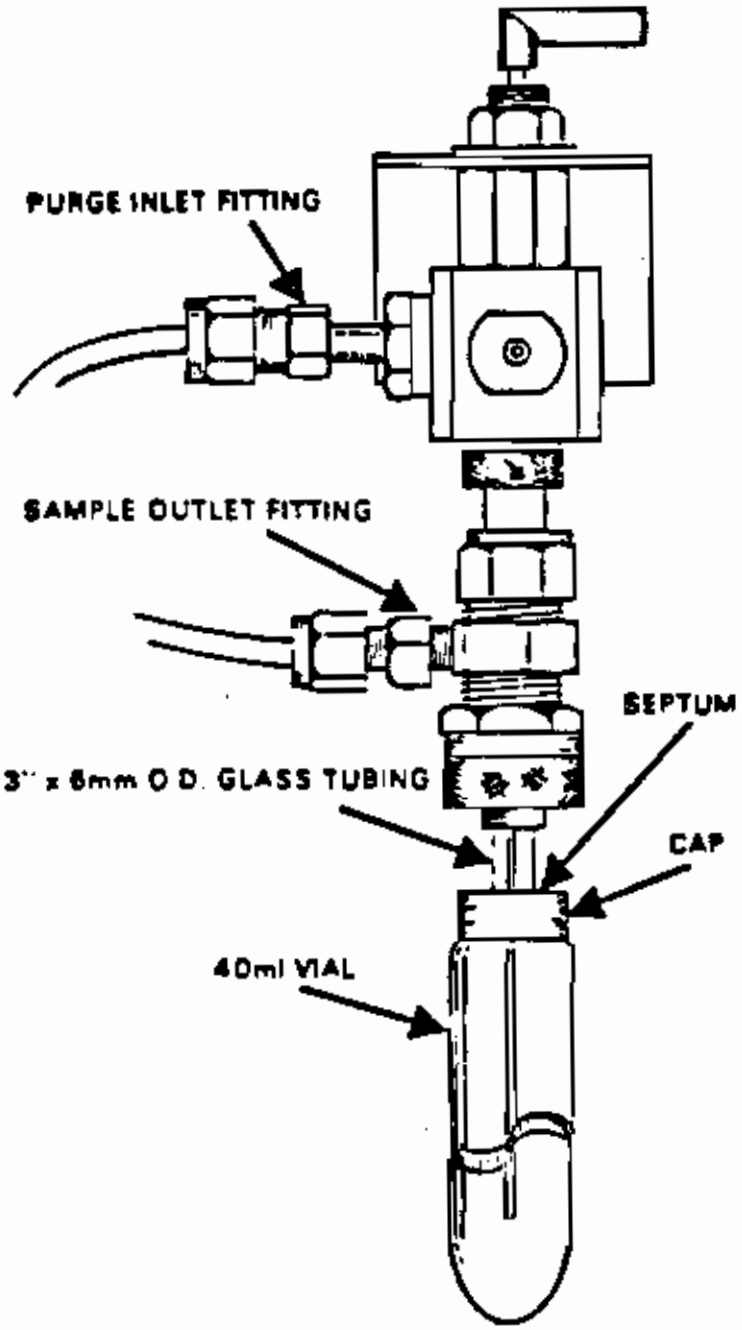


Figure 5. Low Soils Impinger

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

1.7.1.7 Add 10.0 uL of the surrogate spiking solution (1.4.6) and 10.0 uL of the internal standard spiking solution (1.5.3.2) 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 5mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

1.7.1.8 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.

1.7.1.9 Close both valves and purge the sample for 12.0 $\pm$ 0.1 minutes at ambient temperature.

1.7.1.10 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 mL/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.

1.7.1.11 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 carry-over of pollutent compounds.

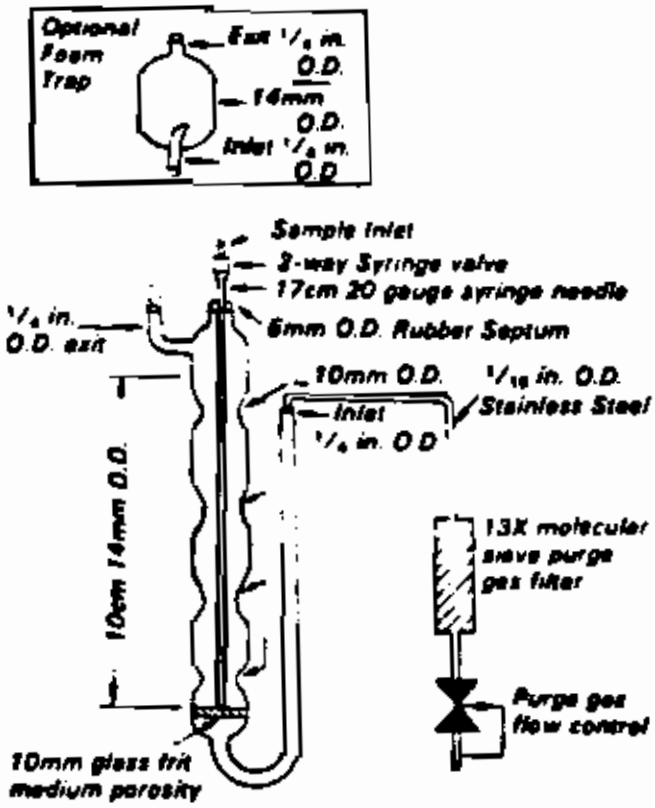


Figure 1. *Purging device*

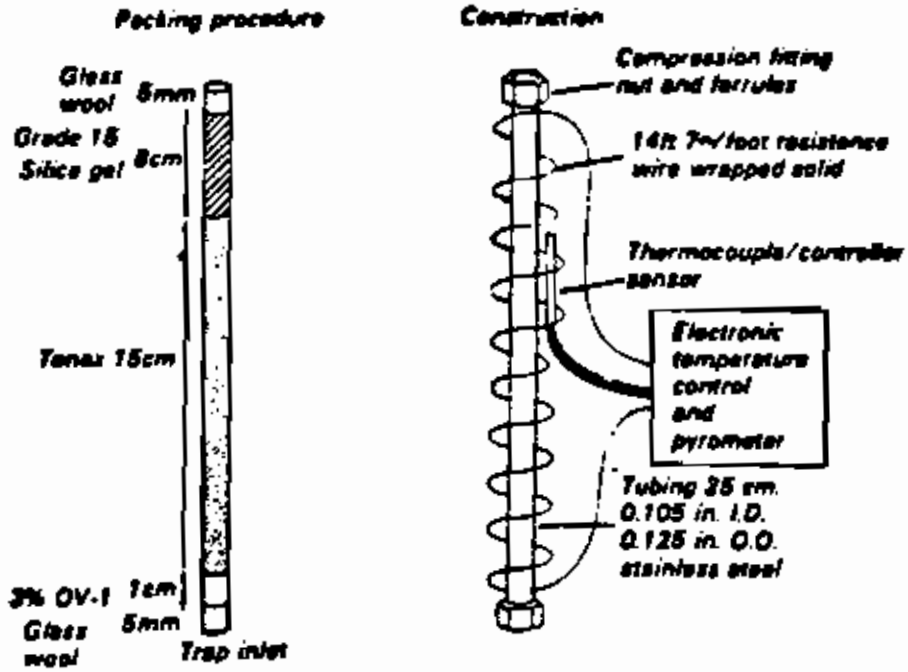


Figure 2. *Trap packings and construction to include desorb capability*

1.7.2 Sediment/Soil Samples

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

- o Assume the sample is low level and analyze a 5 gram sample
- o Use the X factor calculated from the optional Hexadecane screen (Section III), paragraph 1.7.2.1.3

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

1.7.2.1 Low Level Method

The low level method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and internal standards.

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

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

1.7.2.1.1 The GC/MS system should be set up as in 1.7.1.2 - 1.7.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and sample.

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

- o Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- o Recalculate the sample data if any of the above checks reveal a problem.
- o Reanalyse the sample if none of the above are a problem.
- o Report the data from both analyses along with the surrogate data from both.

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

Percent moisture

$$\frac{\text{gm of sample} - \text{gm of dry sample}}{\text{gm of sample}} \times 100 = \% \text{ moisture}$$

1.7.2.1.4 Add the spiked reagent water to the purge device and connect the device to the purge and trap system. NOTE: Steps 1.7.2.1.2 - 1.7.2.1.3, prior to the attachment of the purge device, must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

1.7.2.1.5 Heat the sample to 40°C ± 1°C and purge the sample for 12 ± 0.1 minutes.

1.7.2.1.6 Proceed with the analysis as outlined in 1.7.1.10 - 1.7.1.13. Use 5 mL of the same reagent water as the reagent blank.

1.7.2.1.7 For low level sediment/soils add 10 uL of the matrix spike solution (1.4.7) to the 5 mL of water (1.7.2.1.2). The concentration for a 5 gram sample would be equivalent to 50 ug/kg of each matrix spike standard.

1.7.2.2 Medium Level Method

The medium level method is based on extracting the sediment/soil 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 gram sample was analyzed, the medium level method must be used.

EICP area of the characteristic ions of analytes listed in Tables 2 and 3 are used. The response factor (RF) from the daily standard analysis is used to calculate the concentration in the sample. Use the response factor as determined in paragraph 1.5.3.3 and the following equations:

Water (low and medium level)

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

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)

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

Sediment/Soil (low level)

$$\text{Concentration} \quad \text{ug/kg} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)(D)}$$

(Dry weight basis)

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 (gm) or purged

The addition of a 100 uL aliquot of each of these extracts in paragraph 1.7.2.2.6 will give a concentration equivalent to 6,200 ug/kg of each surrogate standard.

1.7.2.2.4 The GC/MS system should be set up as in 1.7.1.2 - 1.7.1.4. This should be done prior to the addition of the methanol extract to reagent water.

1.7.2.2.5 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.

(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 abundance must be between 30 and 70 percent).

(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.

1.8.2 A library search shall be executed for Non-HSL sample components for the purpose of tentative identification. For this purpose, the most recent available version of the EPA/NIH Mass Spectral Library shall be used. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

1.8.2.1 Up to 10 substances of greatest apparent concentration not listed in Exhibit C for the purgeable organic fraction shall be tentatively identified via a forward search of the EPA/NIH 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.

1.8.2.2 Guidelines for making tentative identification: (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.

1.7.2.2.6 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 1.7.2.2.5 and a volume of methanol solvent to total 100 uL (excluding methanol in standards).

1.7.2.2.7 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.

1.7.2.2.8 Proceed with the analysis as outlined in 1.7.1.9 - 1.7.1.13. 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.

1.7.2.2.9 For a matrix spike in the medium level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (1.4.6), and 1.0 mL of matrix spike solution (1.4.7) in paragraph 1.7.2.2.2. This results in a 6,200 ug/kg concentration of each matrix spike standard when added to a 4 gm sample. Add a 100 uL aliquot of this extract to 5 mL of water for purging (as per paragraph 1.7.2.2.6).

1.7.2.2.6 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 1.7.2.2.5 and a volume of methanol solvent to total 100 uL (excluding methanol in standards).

1.7.2.2.7 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.

1.7.2.2.8 Proceed with the analysis as outlined in 1.7.1.9 - 1.7.1.13. 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.

1.7.2.2.9 For a matrix spike in the medium level sediment/soil samples, add 8.0 mL of methenol, 1.0 mL of surrogate spike solution (1.4.6), and 1.0 mL of matrix spike solution (1.4.7) in paragraph 1.7.2.2.2. This results in a 6,200 ug/kg concentration of each matrix spike standard when added to a 4 gm sample. Add a 100 uL aliquot of this extract to 5 mL of water for purging (as per paragraph 1.7.2.2.6).

(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 abundance must be between 30 and 70 percent).

(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.

1.8.2 A library search shall be executed for Non-HSL sample components for the purpose of tentative identification. For this purpose, the most recent available version of the EPA/NIH Mass Spectral Library shall be used. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

1.8.2.1 Up to 10 substances of greatest apparent concentration not listed in Exhibit C for the purgeable organic fraction shall be tentatively identified via a forward search of the EPA/NIH 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.

1.8.2.2 Guidelines for making tentative identification: (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.

The addition of a 100 uL aliquot of each of these extracts to peragraph 1.7.2.2.6 will give a concentration equivalent to 6,200 ug/kg of each surrogate standard.

1.7.2.2.4 The GC/MS system should be set up as in 1.7.1.2 - 1.7.1.4. This should be done prior to the addition of the methanol extract to reagent water.

1.7.2.2.5 The following table can be used to determine the volume of methenol 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.

EICP area of the characteristic ions of analytes listed in Tables 2 and 3 are used. The response factor (RF) from the daily standard analysis is used to calculate the concentration in the sample. Use the response factor as determined in paragraph 1.5.3.3 and the following equations:

Water (low and medium level)

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

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)

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

Sediment/Soil (low level)

$$\text{Concentration} \quad \text{ug/kg} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)(D)}$$

(Dry weight basis)

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 (gm) or purged

$$\text{Percent moisture} = \frac{\text{gm of sample} - \text{gm of dry sample}}{\text{gm of sample}} \times 100 = \% \text{ moisture}$$

1.7.2.1.4 Add the spiked reagent water to the purge device and connect the device to the purge and trap system. NOTE: Steps 1.7.2.1.2 - 1.7.2.1.3, prior to the attachment of the purge device, must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

1.7.2.1.5 Heat the sample to 40°C ± 1°C and purge the sample for 12 ± 0.1 minutes.

1.7.2.1.6 Proceed with the analysis as outlined in 1.7.1.10 - 1.7.1.13. Use 5 mL of the same reagent water as the reagent blank.

1.7.2.1.7 For low level sediment/soils add 10 uL of the matrix spike solution (1.4.7) to the 5 mL of water (1.7.2.1.2). The concentration for a 5 gram sample would be equivalent to 50 ug/kg of each matrix spike standard.

1.7.2.2 Medium Level Method

The medium level method is based on extracting the sediment/soil 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 analysed by the medium level method. If saturated peaks occurred or would occur when a 1 gram sample was analyzed, the medium level method must be used.

1.9.3.2 If recovery is not withio limits, the following is required:

- o Check to be sure there are oo errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- o Recalculate the sample data if any of the above checks reveal a problem.
- o Reanalyze the sample if none of the above are a problem.
- o Report the data from both analyses along with the surrogate data from both.

Table 2
Characteristic Ions for Surrogate and
Internal Standards for Volatile Orgenic Compounds

Compound	Primary Ion	Secoodary 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-Difluorohenzene	114	63, 88
Chlorobenzene d-5	117	82, 119

1.7.2 Sediment/Soil Samples

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

- o Assume the sample is low level and analyze a 5 gram sample
- o Use the X factor calculated from the optional Hexadecane screen (Section III), paragraph 1.7.2.1.3

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

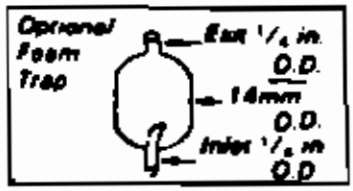
1.7.2.1 Low Level Method

The low level method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and internal standards.

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

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

1.7.2.1.1 The GC/MS system should be set up as in 1.7.1.2 - 1.7.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and sample.



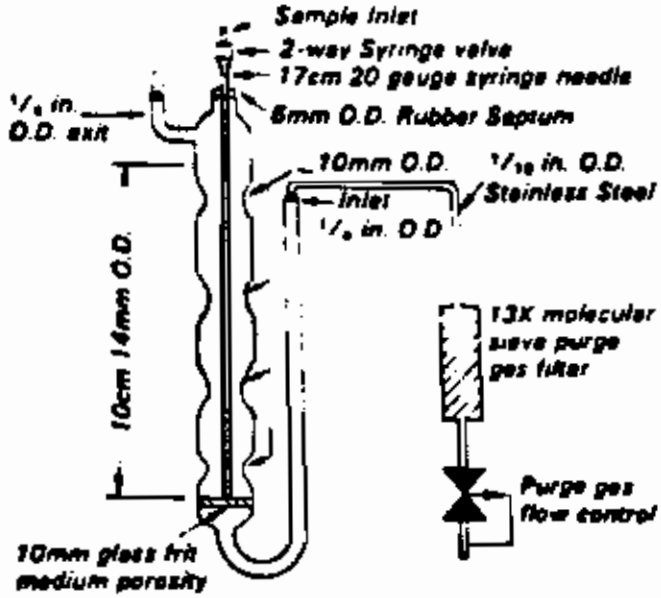


Figure 1. *Purging device*

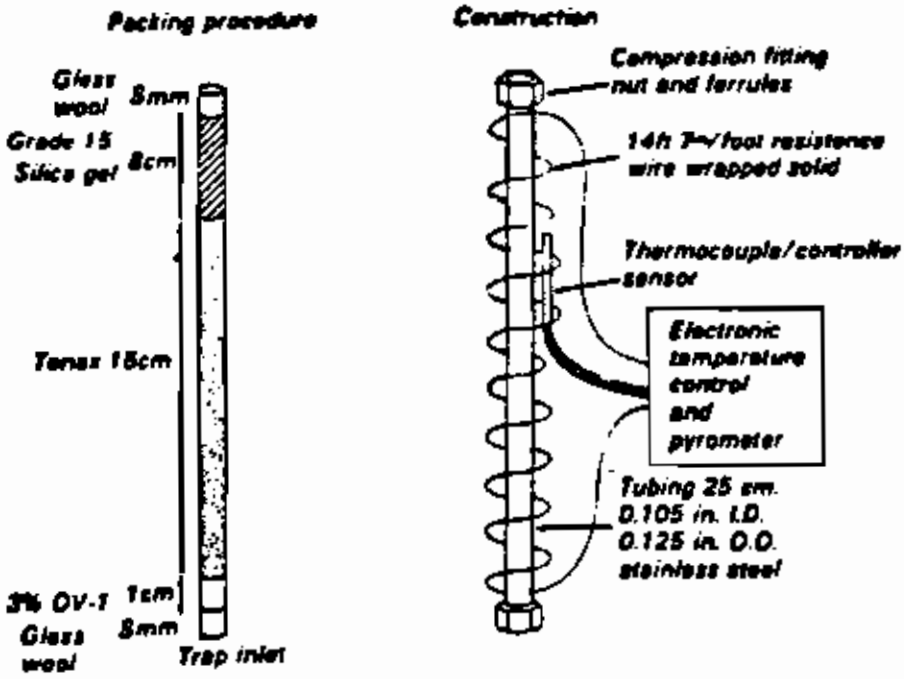


Figure 2. *Trap packings and construction to include desorb capability*

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

1.7.1.7 Add 10.0 uL of the surrogate spiking solution (1.4.6) and 10.0 uL of the internal standard spiking solution (1.5.3.2) 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 5mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

1.7.1.8 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.

1.7.1.9 Close both valves and purge the sample for 12.0 $\pm$ 0.1 minutes at ambient temperature.

1.7.1.10 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 mL/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.

1.7.1.11 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 carry-over of pollutant compounds.

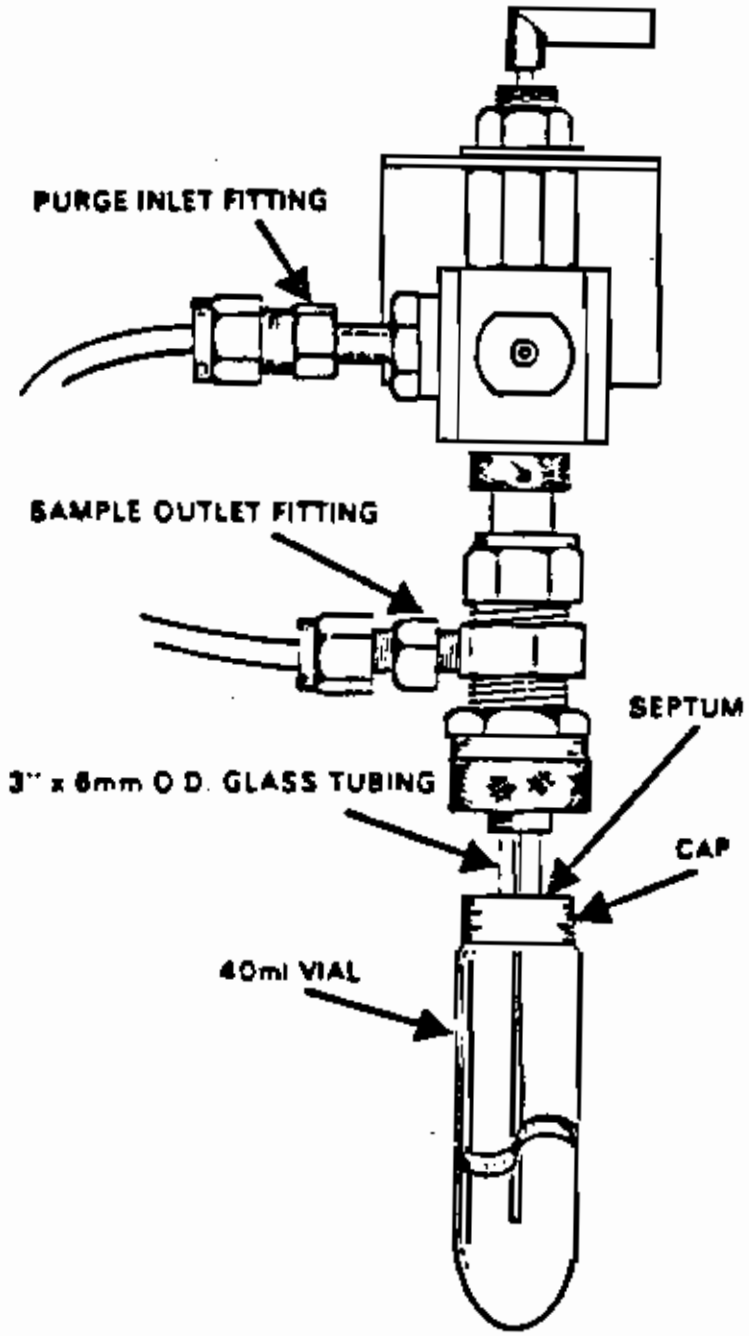


Figure 5. Low Soils Impinger

1.7 Sample Analysis

1.7.1 Water Samples

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

1.7.1.2 Recommended operating conditions for the gas chromatograph - Column conditions: Carhopak B (60/80 mesh with 1% SP-1000 pakced in a 6 foot by 2 mm ID glass column with helium carrier gas at a flow rate of 30 mL/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.

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

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

1.7.1.5 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

2.2.1.4 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.

2.3 Reagents

2.3.1 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.

2.3.2 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.

2.4 Calibration

2.4.1 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standard solutions be stored at 4°C or less in screw cap amber bottles

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.

1.5.3.4 The average response factor (RF) 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 response factor. These compounds (the SPCC) are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. Five compounds (the calibration check compounds, CCC) are used to evaluate the curve. Calculate the % Relative Standard Deviation (%RSD) of RF 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.

1.5.3.5 Check of the calibration curve should be performed once every 12 hours. These criteria are described in detail in the instructions for Form VII, Continuing Calibration Check. The minimum response factor for the system performance check compounds must be checked. If this criteria is met, the response factor of all

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).

2.4.4.1 The average response factor (RF) should 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 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 Date for more details.

2.4.4.2 A % Relative Standard Deviation (%RSD) is calculated for thirteen compounds labeled the Calibration Check Compounds (CCC). A maximum % RSD is also specified for these compounds. These criteria must be met for the calibration curve to be valid.

2.4.5 Check of the calibration curve must be performed once every 12 hours during analysis. These criteria are described in detailed in the instructions for Form VII, Calibration Check. The minimum response factor for the system performance check compounds must be checked. If this criteria is met, the response factor of all compounds is calculated. A percent difference of the daily response factor (12 hour) compared to the average 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.

2.4.6 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

1.4.7 Purgeable Organic Matrix Standard Spiking Solution

1.4.7.1 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

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

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

1.4.9 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standard solutions be stored at -10°C to -20°C in screw cap amber bottles with reflon liners.

1.5 Calibration

1.5.1 Assemble a purge and trap device that meets the specification in paragraph 1.3.6. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, daily condition traps 10 minutes while backflushing at 180°C with the column at 220°C.

1.5.2 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 1.7.1.2 Calibrate the purge and trap-GC/MS system using the internal standard technique (paragraph 1.5.3).

Initial Column Temperature Hold	- 30°C for 4 minutes
Column Temperature Program	- 30-300°C at 8 degrees/min.
Final Column Temperature Hold	- 300°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/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 any compound saturates the detector, the extract must be diluted and reanalyzed. See "Sample Analysis" in Exhibit E.

2.6 Qualitative Analysis

2.6.1 The target compounds listed in the Hazardous Substances List (HSL), Exhibit C, shall be identified 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 componeot and standard component mass spectra.

2.6.1.1 For establishing correspondance of the GC relxtive rateotion time (RRT), the sample component RRT must compare within $\pm$ 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. The RRT should be assigned by using extracted ion currsot profiles for ions unique to the component of interest.

1.4.3 Methanol - Pesticide quality or eqvuivalent.

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

1.4.4.1 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.

1.4.4.2 Add the assayed reference material as described below.

1.4.4.2.1 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.

1.4.4.2.2 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.

2.6.2.1 Up to 20 substances 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 EPA/NIH 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 interpretetion specialist assign a tentative identification. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

2.6.2.2 Guidelines for making tentative identification:

(1) Relntive intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant iou) should he present in the sample spectrum.

(2) Tha relative intensities of the major ions should egree within ± 20%. (Example: For an ion with an abundance of 50% in the standerd spectra, the correesponding sample ion abundance must be between 30 and 70 percent.

(3) Moleculor ions present in reference spectrum should he present in sample spectrum.

(4) Ious present in the sample spectrum but not in rhe reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(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. Data system lihrary reduction programs can sometimes create these discrepancies.

1.3.6.4 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.

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

1.3.7 GC/MS system

1.3.7.1 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.

1.3.7.2 Column - 6 ft long x 0.1 in ID glass, packed with 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent.

1.3.7.3 Mass spectrometer - Capable of scanning from 35 to 260 amu every seven 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.

1.3.7.4 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.

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.)

Sediment/soil

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

(Dry weight basis)

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 8 mL extract to 0.8 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)

1.2.3 Contamination by carry over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry over, 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.

1.3 Apparatus and Materials

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

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

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

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

1.3.5 Glassware

1.3.5.1
- Bottle - 15 mL, screw cap, with Teflon cap liner.
- Volumetric flasks - class A with ground-glass stoppers.
- Vials - 2 mL for GC autosampler.

Table 4.
Characteristic Ions for Semivolatile HSL Compounds

Parameter	Primary Ion	Secondary Ion(s)
N-Nitrosodimethylamine	42	74, 44
Phenol	94	65, 66
Aniline	93	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	122	107, 121
Benzoic Acid	122	105, 77
bis(-2-Chloroethoxy)Methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobeozene	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-Chloronaphthelene	162	164, 127
2-Nitroaniline	65	92, 138
Dimetnyl Phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dioitrophenol	184	63, 154
4-Nitrophenol	139	109, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	89	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141

(continued)

1. GC/MS Analysis of Purgeable Organics

1.1 Summary of Methods

1.1.1 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.

1.1.2 Sediment/Soil Samples

1.1.2.1 Low Level. An inert gas is bubbled through a mixture of a 5 gm sample and reagent water contained in a suggested specially designed purging chamber (illustrated on page D-95) 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.

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
Endrin Aldehyde	67	345, 250
Endosulfan Sulfate	272	387, 422
4,4'-DDT	235	237, 165
Methoxychlor	227	228
Chlordane	373	375, 377
Toxaphene	159	231, 233
Arochlor-1016	222	260, 292
Arochlor-1221	190	222, 260
Arochlor-1232	190	222, 260
Arochlor-1242	222	256, 292
Arochlor-1248	292	362, 326
Arochlor-1254	292	362, 326
Arochlor-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-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_8	164	162, 160
Phenanthrene-d_8	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265

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

2.6.2.2.3 A separate medium level extract is prepared for Pesticide/PCBs as described in Section 11 C, paragraph 1.7.2.

2.6.2.3 Peaks are detected at greater than 100% full scale deflection:

2.6.2.3.1 If the screen is from the medium level preparation, calculate the dilution necessary to reduce the major peaks to between 50% and 100% full scale deflection. Use this dilution factor to dilute the extract. This dilution is analyzed by GC/MS for extractable organics.

2.6.2.3.2 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.

2.7 GC/MS Analysis

2.7.1 Use the information from 2.6 to perform the GC/MS analysis of extractables in Section IV, ANALYSIS, paragraph 2.

NOTE: The 2mm ID column cited on page D-124 as Column 1 will not adequately separate dibutyl chlorendate and endrin.

3.3.1.1.2 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.

3.3.1.2 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 equivalent).

3.3.2 Balance-analytical capable of accurately weighing 0.0001 g.

3.4 Reagents

3.4.1 Isooctane (2,2,4-trimethylpentane), hexane, and toluene - Pesticide quality or equivelent.

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

3.4.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams 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 EMLS/LV supplied standards.

2.3.2.2 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 componnd. The storage and stability requirements ere the same as specified in 2.3.2.1.2.

2.4 GC Calibration

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

2.4.1.1 Standardized for 50% full scale response from 50 ng of phenanthrane.

2.4.1.2 Adeqnately separetes phenol from the solvent front.

2.4.1.3 Minimum of 25% full scale response for 50 ng of di-n-octylphthalate.

2.5 GC/FID Screening

2.5.1 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 Temperatura Hold - 280°C for 8 minutes
Injector - Grob-type, splitless
Sample Volume - 1 uL - 2 uL
Carrier Gas - Helinm at 30 cm/sec

2.5.2 Inject the GC calibration standard and ensure the criteria specified in 2.4 are met before injecting samples. Estimate the response for 10 ng of phenanthrane.

3.5 Calibration

3.5.1 The gas chromatographic system must be calibrated using the external standard technique for all packed columns used for quantitation.

3.5.2 External standard calibration procedure:

3.5.2.1 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 MDL 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.

3.5.2.2 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.

1.6.3 Sample Analysis

Proceed to Section IV ANALYSES, paragraph 1. "GC/MS Analysis of Purgeables.

2. Screening of Extractable (Semivolatile) Organic Extracts

2.1 Summary of Method

2.1.1 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.

2.2 Apparatus and Materials

2.2.1 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.

2.2.1.1 Above GC equipped with flame ionization detector.

2.2.1.2 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).

2.3 Reagents

2.3.1 Methylene chloride - pesticide residue analysis grade or equivalent.

3.6.1.1 Inject Individual Standard mix A or B and all multi-response pesticides/PCBs at the beginning of each 24 hour sequence. (See paragraph 3.6.2.2.2.) To establish the daily RT window for the pesticides/PCBs 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 or B is analyzed at the beginning, at 12-hour intervals throughout the analysis, and at the end. Any peaticide outside of its established time window requires immediate investigation and correction before continuing the analysis. The laboratory must reanalyze all affected samples.

3.6.1.2 Sample analysis of extracts from Section 11, SAMPLE PREPARATION, can begin when linearity and degradation QA/QC criteria specified in Exhibit E have been met. Analyze groups of 5 samples. Evaluation mix B or the Individual Standard mix A or B must be alternately reanalyzed after each group. If a multi-response pesticide/PCB is detected in either of the preceding groups of 5 samples, the appropriate multi-response pesticide/PCB may be substituted for Individual mix A or B. The alternating standard's ratios of the response to the amount injected must be within 15% of each other (20% for confirmation runs). Deviations larger than 15% require the laboratory to repeat the samples analyzed in between. The 15% criteria pertains only to compounds being quantitated. Samples must also be repeated if the degradation of DDT and/or endrin exceeds 20% respectively on the daily intermittent analysis of Evaluation standard mix B.

1.5.2 Inject the same volume of hexadecane extract as the extracted standard mixture in 1.5.1. Use the GC conditions specified in 1.2.1.2.

1.6 Analytical Decision Point

1.6.1 Water

1.6.1.1 Compare the hexadecane sample extract chromatograms against the reagent blank and extracted standard chromatograms.

1.6.1.1.1 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.

1.6.1.1.2 If peaks are present prior to the n-dodecane and the aromatics are distinguishable, follow Option A (1.4.2.1).

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

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

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

IV.

24-Hour Sequence for Pesticide/PCB Analysis:

Sample or Standard

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. Tech. chlordane
8. Aroclors 1016/1260
9. Aroclor 1221
10. Aroclor 1232
11. Aroclor 1242
12. Aroclor 1248
13. Aroclor 1254
14. 5 samples
15. Evaluation standard mix B
16. 5 samples
17. Individual standard mix A or B
18. 5 samples
19. Repeat the above sequence starting with Evaluation Standard Mix B (step 15 above).
20. Pesticide/PCB analysis sequence must end with Individual Standard mix A or B regardless of number of samples analyzed.

* These may be one mixture (see paragraph 3.4.3).

1. Screening of Hexadecane Extracts for Purgeables

1.1 Summary of Method

1.1.1 The hexadecane extracts of water and sediment/soil 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.

1.2 Apparatus and Materials

1.2.1 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.

1.2.1.1 Above GC equipped with flame ionization detector.

1.2.1.2 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.

1.3 Reagents

Hexadecane - pesticide residue analysis grade or equivalent.

1.4 Limitations

1.4.1 The flame ionization detector varies considerably in sensitivity when comparing aromatics and halogenated methanes and ethanes. Halomethanes are approximately 20 X less sensitive

3.6.3.2 Tentative identification is when the unknown's retention time matches the retention time of a corresponding standard that was chromatographed within a 24 hour period.

3.6.3.3 Determine if any pesticides/PCBs listed in Table 7 are present. The PCB chromatograms in Figure 6-12 should be helpful for pattern recognition.

3.6.3.3.1 If the response for any of these compounds is 100% or less of full scale, the extract is ready for confirmation and quantitation.

3.6.3.3.2 If the response for any compound is greater than 100% of 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.

3.6.3.3.3 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.

3.6.3.3.4 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.

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

- o pulling the emulsion through a small plug of Pyrex glass wool packed in a pipet, or
- o transferring the emulsion to a centrifuge tube and centrifuging for several minutes.

6.1.3 Add 200 uL of working standard mixture #1 and #2 to separate 40 mL portions of reagent water. Follow steps 6.1.1 - 6.1.2 beginning with the immediate addition of 2.0 mL of hexadecane.

6.2 Sediment/Soil

6.2.1 Add approximately 10 grams of soil (wet weight) to 40 mL of reagent water in a 50 mL centrifuge tube with a ground glass stopper or teflon-lined cap. Cap and shake vigorously for one minute. Centrifuge the capped flask briefly. Quickly transfer supernatent water to a 50 mL volumetric flask equipped with a ground glass stopper.

6.2.2 Follow 6.1.1, starting with the addition of 2.0 mL of hexadecane.

7. Sample Analysis

The sample is ready for GC/FID Screening. Proceed to Section III, SCREENING, paragraph 1, screening of Hexadecane Extracts for Purgeables.

3.7.2 Table 7 provides examples of operating conditions for the gas chromatograph. Separation should be ≥ 25% resolution between peaks. This criteria must be considered when determining whether to quantitate on the Primary Analysis or the Confirmation Analysis. When this criteria cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

All QC specified in Exhibit E must be adhered to, i.e., the ≥ 12 min. 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.

3.7.3 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. One 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. The detector attenuation must provide peak response equivalent to the Primary Analysis response for each compound to be confirmed.

3.7.3.1 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.

3.7.3.1.1 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% RSD, use the appropriate equation in paragraph 3.8 for calculation.

3. Interferences

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 as described in paragraph 8.5. 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 industrial complex or municipality being sampled.

4. Apparatus and Materials

4.1 Vials and caps, 2 mL for GC auto sampler.

4.2 Volumetric flask, 50 mL with ground glass stopper.

4.3 Pasteur pipets, disposable.

4.4 Centrifuge tube, 50 mL with ground glass stopper or Teflon-lined screw cap.

4.5 Balance - Analytical, capable of accurately weighing 0.0001 gm.

5. Reagents

5.1 Hexadecane and methanol-pesticide residue analysis grade or equivalent.

5.2 Reagent water - Reagent water is defined as water in which an interferent is not observed at the MDL of each parameter of interest.

5.3 Standard mixture #1 containing benzene, toluene, ethyl benzene and xylene. Standard mixture #2 containing n-nonane and n-dodecane.

If none of the DDT series is to be quantitated and DDT exceeds the 10% RSD, simply record the % RSD on the proper form. Any time toxaphene is to be quantitated, follow 3.7.3.1.1.

3.7.3.2 After the linearity standards required in 3.7.3.1 are injected, continue the confirmation analysis injection sequence with all compounds tentatively identified in 3.6, to establish the daily retention time windows. (See paragraph 3.6.1.1.) Analyze all confirmation standards for a case at the beginning, at intervals specified in 3.7.3.3, 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 following the standard that exceeds the criteria.

3.7.3.3 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 each 10 samples). The alternating standard's ratios of the response to the amount injected must be within 15% of each other if quantitation is performed. Deviations larger than 15% require the laboratory to repeat the samples analyzed following the standard that exceeds the criteria. The 15% criteria only pertains to compounds being quantitated.

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.

2.8.3.3 Add 5 mL distilled water and shake for at least 1 min. Allow the sample to stand for 5-10 min. and remove the hexane layer (top) for analysis. Concentrate the hexane to 1.0 mL as per paragraphs 2.7.1 and 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 column technique. Continue as outlined in paragraph 2.8.2.2.

3.7.4.2 Quantitation must be on the packed column chromatogram (primary or confirmation) that provides the best separation from interfering peaks.

3.7.4.2.1 Quantitation of technical chlordane. Weathering and/or different formulations of chlordane may modify the technical chlordane pattern shown in Figure 3. If the chlordane pattern in a sample is similar to Figure 3, use a technical chlordane standard for quantitation. If the pattern is different but gamma and alpha chlordane are present, use gamma and alpha chlordane standards for calculation, total the results, report under technical chlordane but footnote the data as calculated using gamma and alpha chlordane.

3.7.4.3 Computer reproductions of chromatograms manipulated to ensure all peaks are on scale over a 100 fold range is acceptable. However, this can be no greater than a 100 fold range. This is to prevent rerention 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.

3.7.4.4 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" in Section II, B, Sample Preparation for Pesticides/PCBs.

internal wall of the tube must be rinsed down several times with methylene chloride (hexane for pesticides analysis) during the operation, and the final volume brought to 0.8 mL with methylene chloride (hexane for pesticide analysis). 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 was need, this 0.8 mL represents a 2 times dilution to account for only half the extract going through the GPC.

2.7.4 Store all extracts at 4°C in the dark in Teflon-sealed containers until all analyses are performed.

2.8 Pesticide/PCB.

2.8.1 Alumina Column Cleanup

All samples must be taken through this cleanup technique to eliminate BNA surrogates that will interfere in the GC/ECD analysis.

2.8.1.1 Add 3 gm of activity III neutral alumina to the 10 mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

2.8.1.2 Transfer the 1.0 mL of hexane/acetone extract from paragraph 2.7.1 to the top of the alumina using a disposable Pasteur pipet. Collect the eluate in a clean, 10 mL concentrator tube.

2.8.1.3 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 addition and elution of the sample.

V_t = Volume of low level total extract
(Use 20,000 uL or a factor of this when dilutions are made other than those accounted for below):
- o 1/20 total extract taken for pesticide analysis (derived from 0.5 mL of 10 mL extract)
- o final concentration to 1.0 mL for pesticide analysis

- or - V_t = Volume of medium level 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. C.)

W_s = Weight of sample extracted (gm)

3.8.2 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.

3.8.3 Calculation for surrogate and matrix spikes recovery.

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

Where: Q_d = quantity determined by analysis
Q_a = quantity added to sample.

Be sure all dilutions are taken into account. Sediment/soil has a 20 time dilution factor built into the method when accounting for one-twentieth of extract taken for pesticide analysis and final dilution to 1 mL.

3.8.4 Report results in micrograms per liter or micrograms per kilogram without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

2.7 Splitting of Extract and Final Concentration

NOTE: If only pesticide or BNA anlaysis is to be performed on a sample only the appropriate surrogatas for that fraction should be addad as per paragraph 2.5.2.3 (and only appropriate matrix spikes for duplicate matrix spike samplas). The 10 mL extract resulting from paragraph 2.5.8 should not be split as described in paragrxph 2.7.1, following, but should be concentrated as follows: to 1.0 mL for BNAs (not to 0.8 mL as in paragraph 2.7.2). However, for pesticidas/PCBs, fnllow 2.7.1 as written, because of the limited clesnup capacity of the micro alumina column.

The alumina clesn-up for pesticidas is atill required when BNA surrogxtes are not present in order ro remove polsr interferents.

2.7.1 Transfer 0.5 mL of the 10 mL methylene chloride extract to a separate concentrator tube. Add 5 mL of hexane and a silicou carbide boiling chip And mix using vortex mixer. Attach a two-hall micro-Snyder column. Pre-wat the Snyder column by adding 0.5 mL of hexane to tbe top of the column. PlAce the K-D apparatus on a hot water bath (80°-90°C) so that the conceotrator tnbe in

Table 7.

Chromatographic Conditions for Pesticides/PCBs*

Parameter	Typical Retention Time (min) Column 1*	Column 2
alpha-BHC	1.45	1.64
gamma-BHC	1.66	1.94
beta-BHC	2.18	1.76
Heptachlor	2.27	3.21
delta-BHC	2.55	2.01
Aldrin	2.76	4.01
Heptachlor epoxide	4.31	4.98
Endosulfan I	5.46	6.26
4,4'-DDE	6.37	7.51
Dieldrin	6.74	7.38
Endrin	8.25	8.35
4,4'-DDD	10.08	9.53
Endosulfan II	10.14	8.35
4,4'-DDT	12.06	12.75
Endrin aldehyde	13.64	9.53
Endosulfan sulfate	16.73	11.09
Endrin ketone	22.70	-
gamma Chlordane	4.77	5.74
alpha Chlordane	5.24	6.39
Toxaphene	mr	mr
Aroclor-1016	mr	mr
Aroclor-1221	mr	mr
Aroclor-1232	mr	mr
Aroclor-1242	mr	mr
Aroclor-1248	mr	mr
Aroclor-1254	mr	mr
Aroclor-1260	mr	mr
methoxychlor	24.07	19.60
dibutyl chlorendate	21.80	27.21

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.

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.

Capillary column conditions: 30 m x 0.25 mm ID, 0.25 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

*GC conditions for attached chromatograms (not contract requirements)

NOTE: 2mm ID column with 80/100 mesh does not adequately resolve dibutyl chlorendate and endrin ketone.

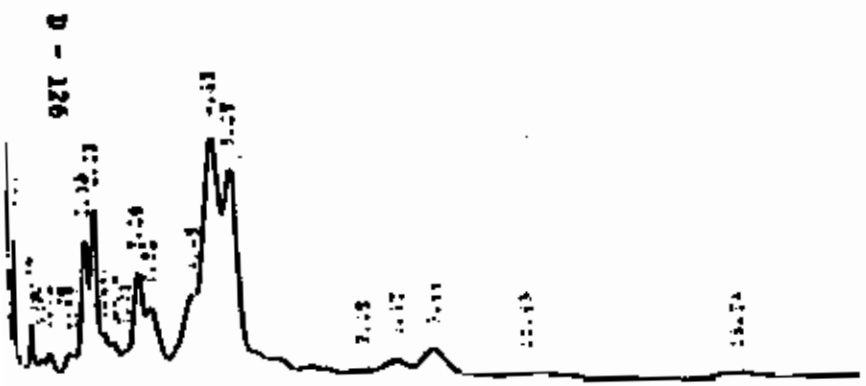


Figure 3. Gas chromatogram of technical chlordane.
See Table 3 for conditions. (1.5% OV-17/1.95% QV-210)

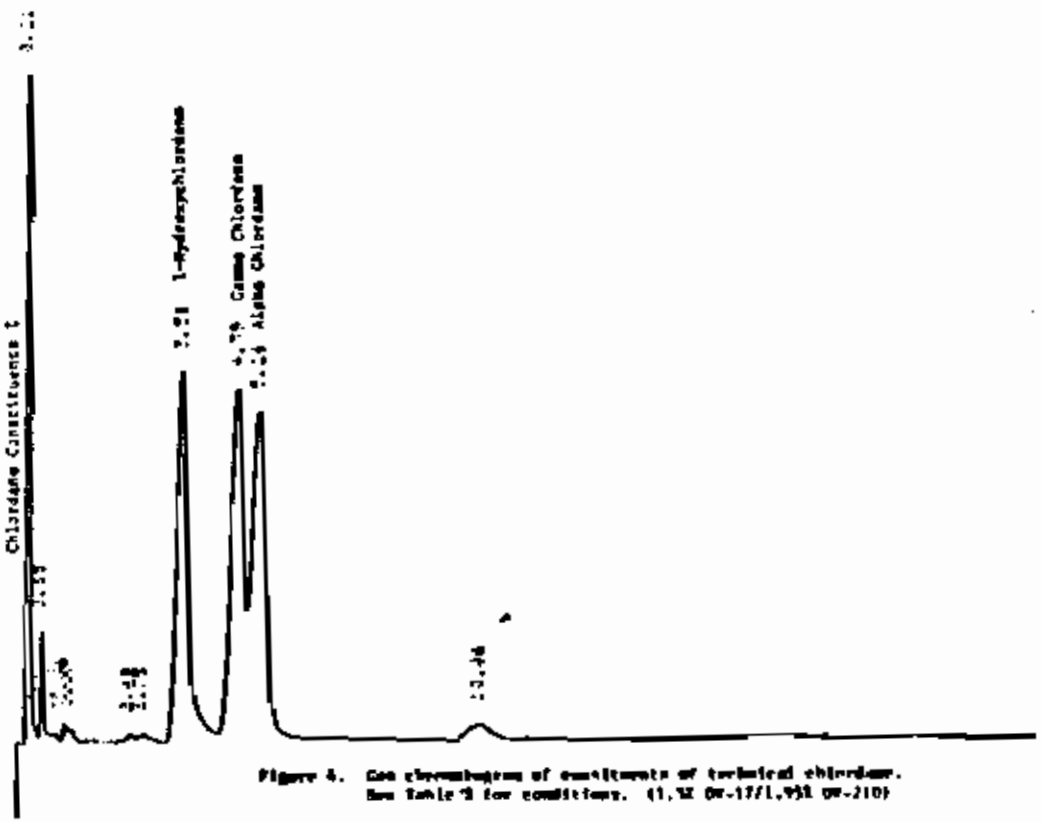


Figure 4. Gas chromatogram of constituents of technical chlordane.
See Table 3 for conditions. (1.5% OV-17/1.95% QV-210)

Figure 1. Gas chromatogram of pesticides
See Table 5 for conditions. (1.5% OV-17/1.95% QV-210)

Figure 1. Gas chromatogram of pesticides
See Table 5 for conditions. (1.5% OV-17/1.5% OV-210)

052

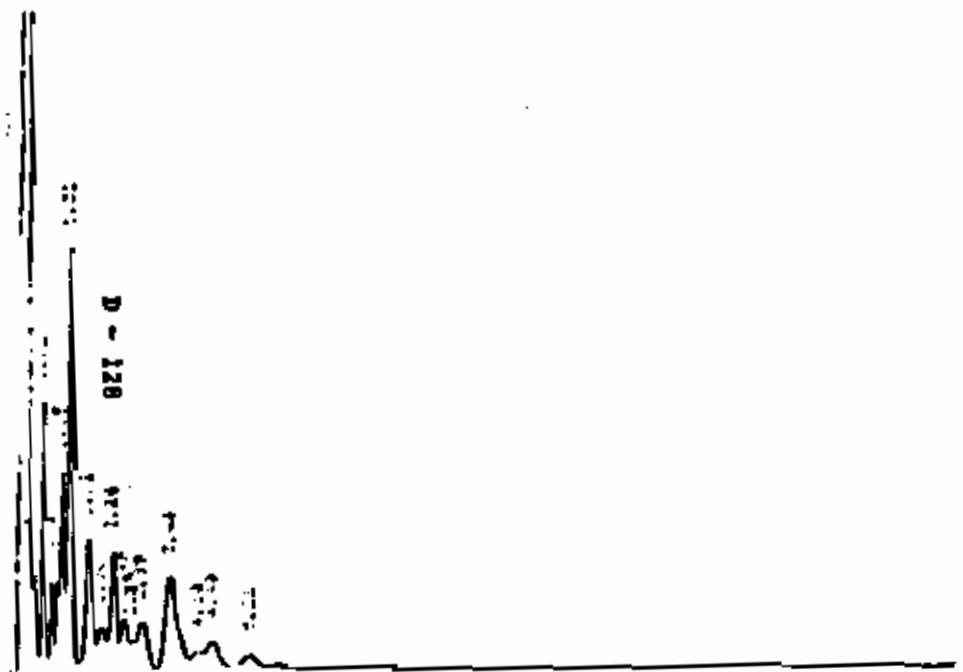


Figure 6. Gas chromatogram of Aroclor 1221.
See Table 1 for conditions. (1.5% OV-17/1.95% OV-210)

054

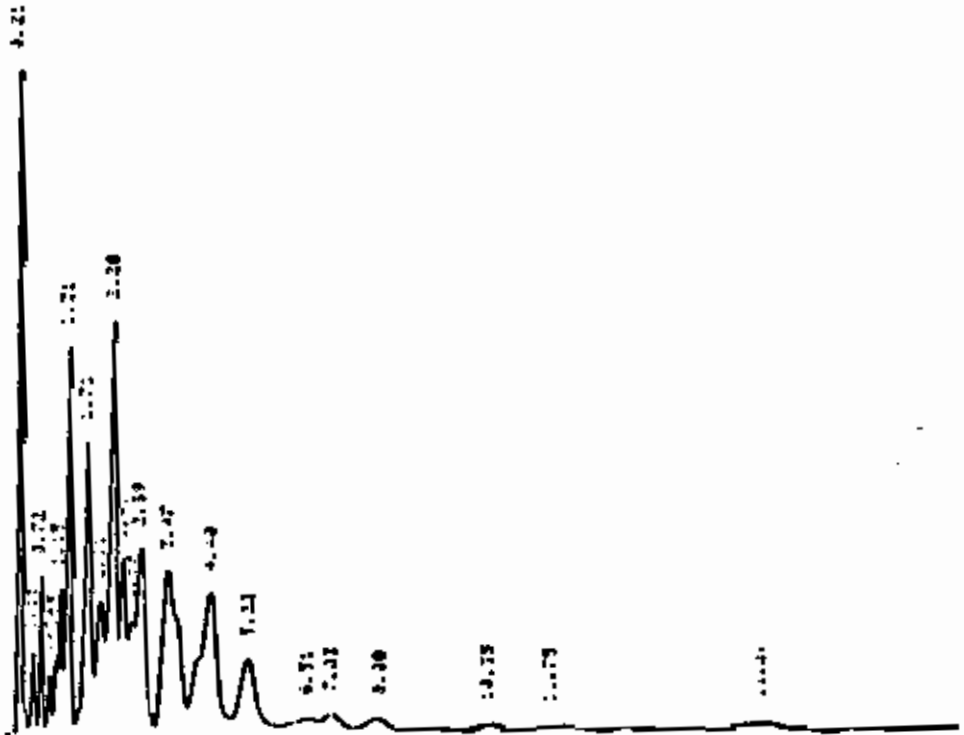


Figure 7. Gas chromatogram of Aroclor 1232.
See Table 1 for conditions. (1.5% OV-17/1.95% OV-210)

5/84

IV.

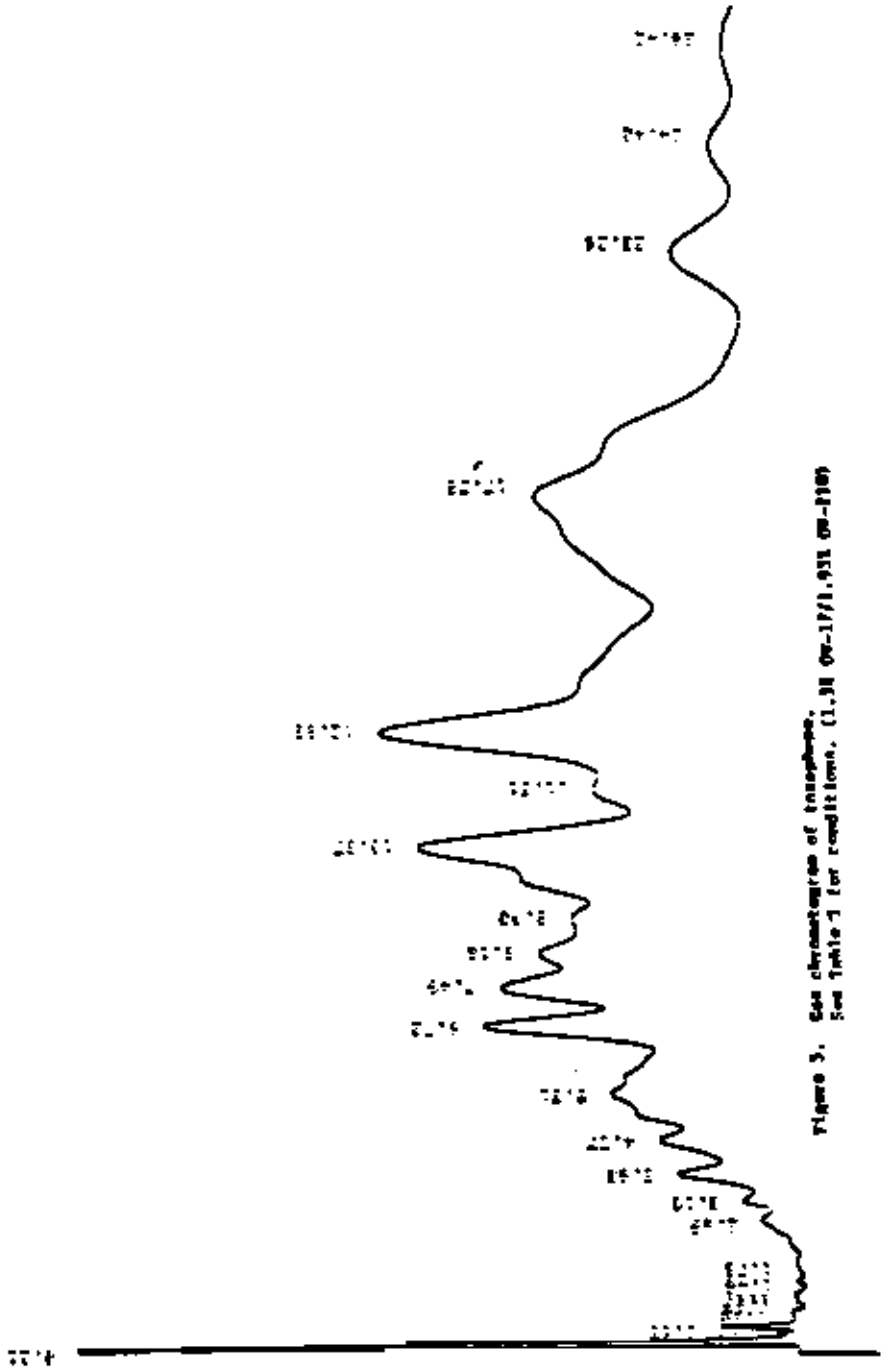


Figure 3. Gas chromatogram of toxaphene. See Table 1 for conditions. (1.3E 06-17/1.93% 08-210)

062

Figure 10. Gas chromatogram of Aroclor 1248.
See Table 7 for conditions. (0.53 OV-17/1.95% OV-210)

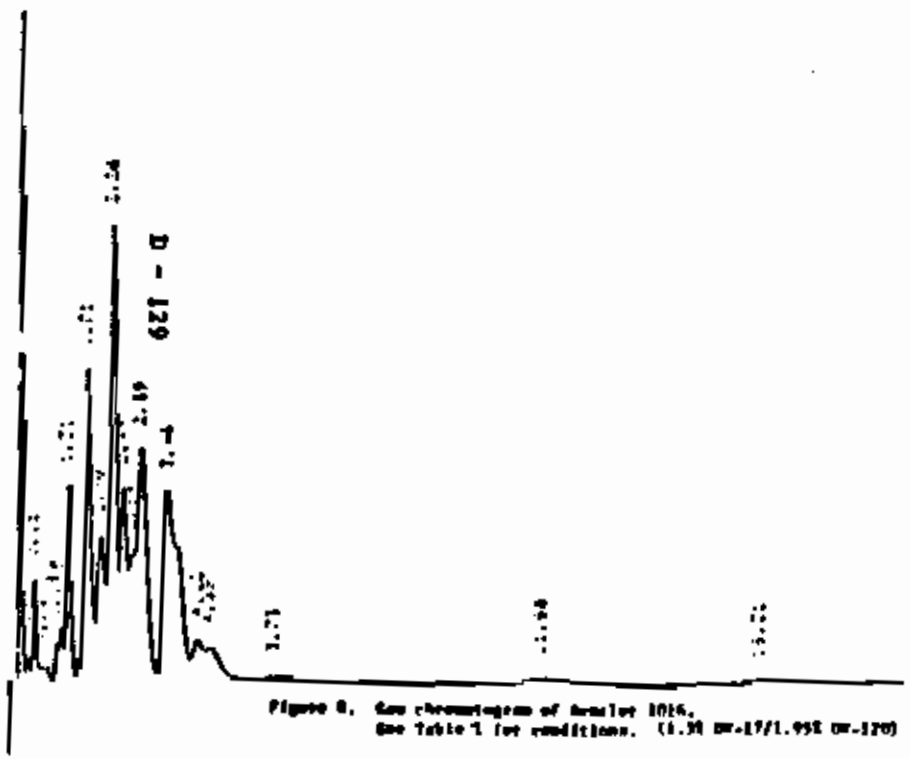


Figure 8. Gas chromatogram of Aroclor 1016.
See Table 1 for conditions. (1.5% OV-17/1.95% QF-120)

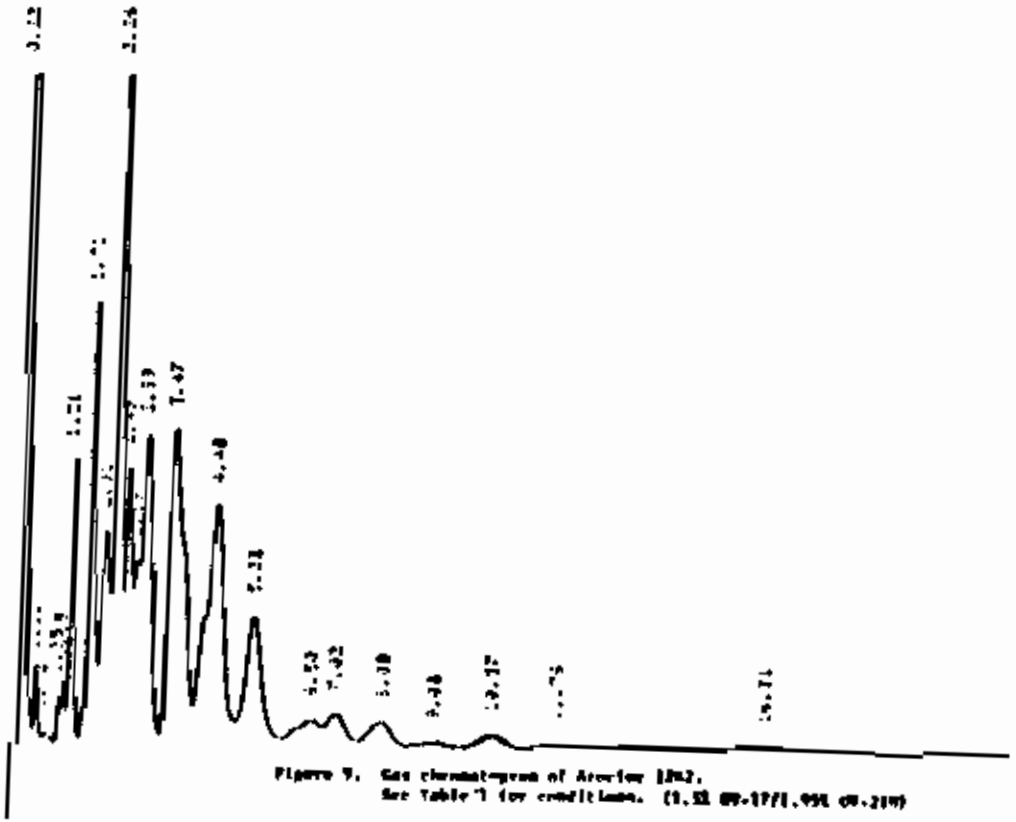


Figure 9. Gas chromatogram of Aroclor 1242.
See Table 1 for conditions. (1.5% OV-17/1.95% QF-210)

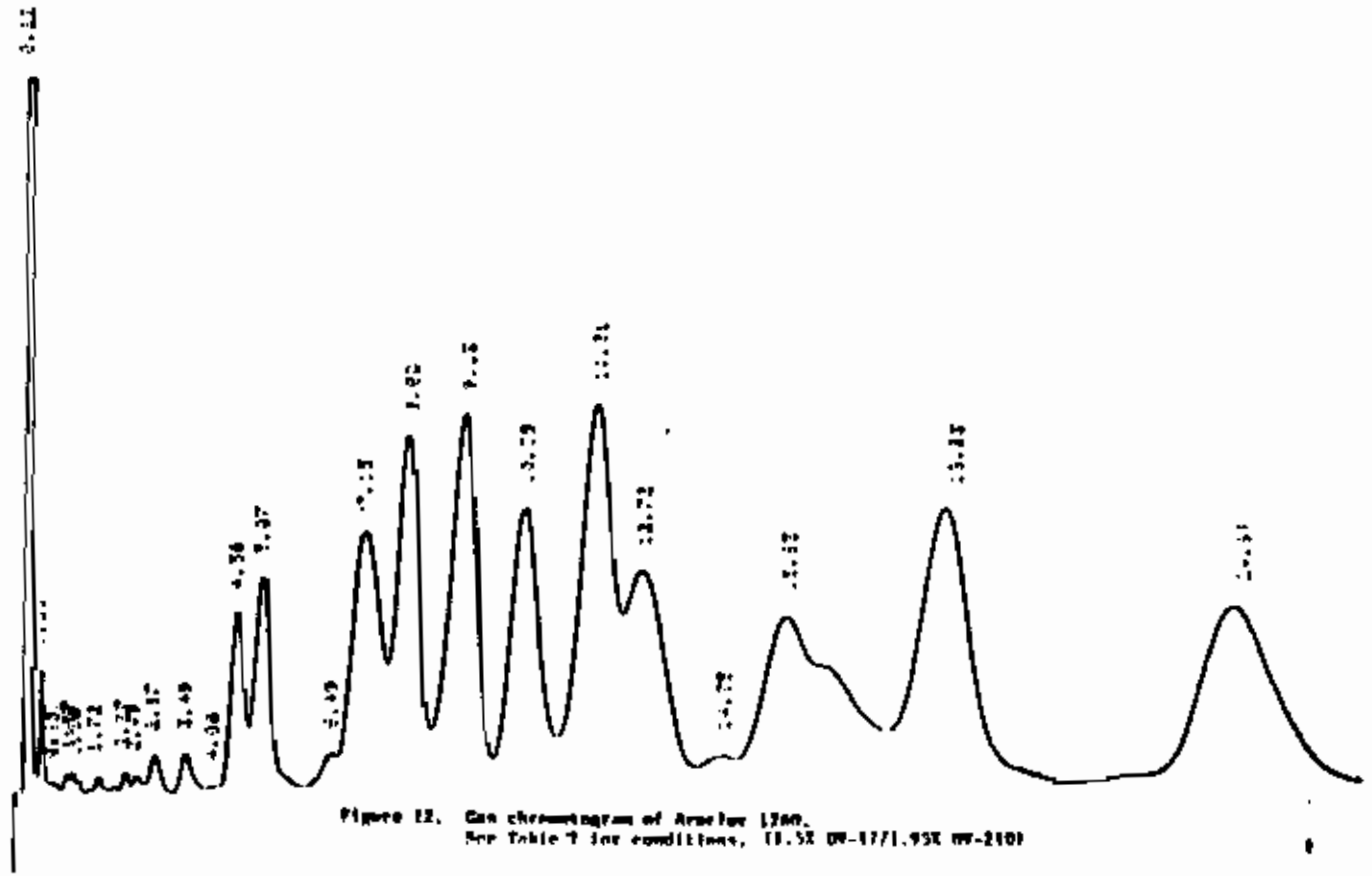


Figure 12. Gas chromatogram of Aroclor 1260.
See Table 7 for conditions. (3.5% OV-17/1.95% OV-210)

059

Figure 11. Gas chromatogram of Aroclor 1254.
See Table 5 for conditions. (1.5% OV-17/1.95% QF-2100)

Figure 14. Chromatogram of all single component pesticides on a fused silica capillary column. See Table 7 for conditions.

TOTAL AREA = 62:054.00
MULTIPLIER = 1

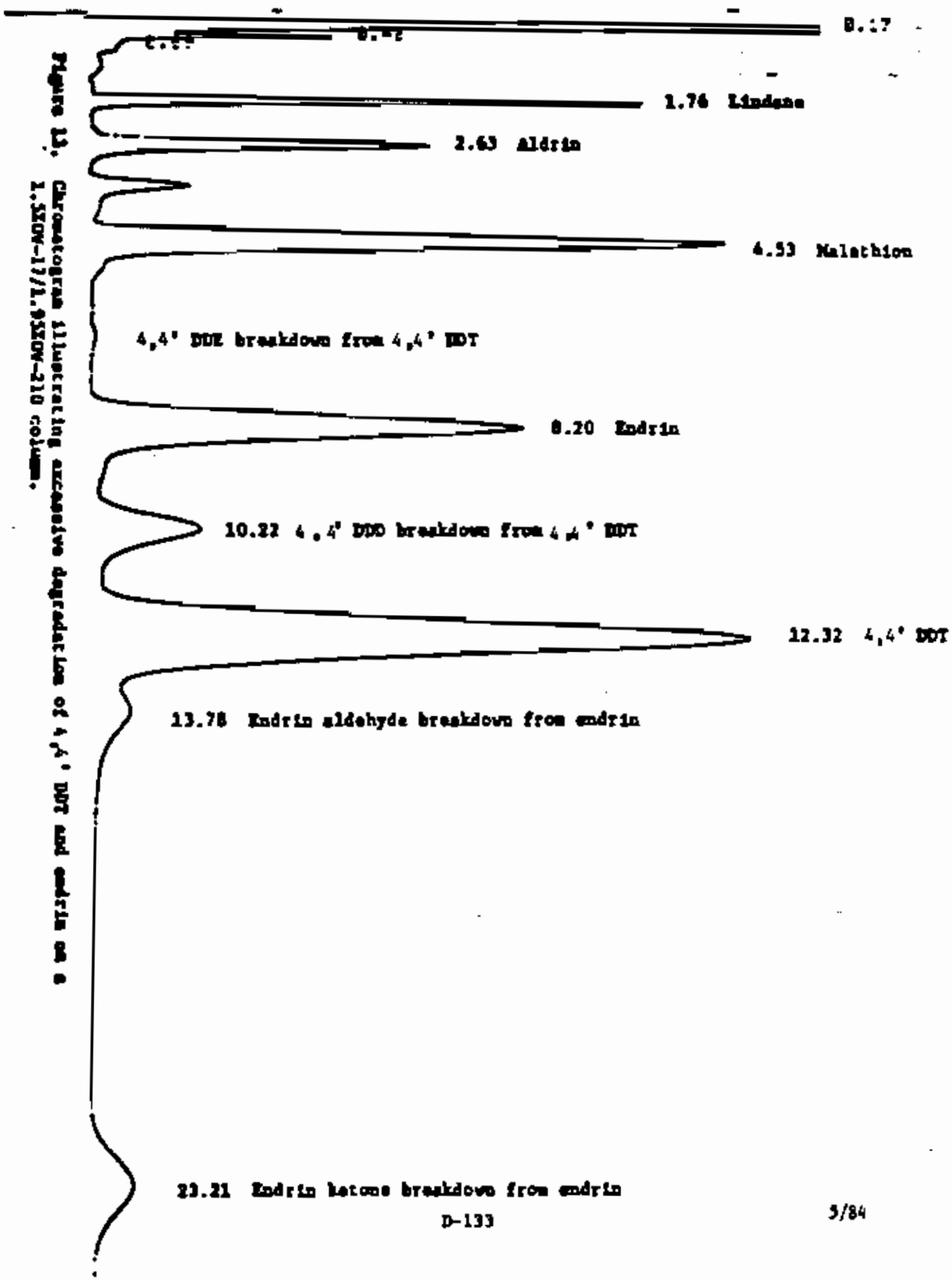


Figure 13. Chromatogram illustrating separation of 4,4' DDT and endrin on a 1.5%OV-17/1.95%OV-210 column.

EXHIBIT E

Quality Assurance/Quality Control Requirements

QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

SECTION I - INTRODUCTION AND SCOPE

The purpose of the Quality Assurance/Quality Control (QA/QC) program outlined here is the definition of procedures for the evaluation and documentation of subsampling, analytical methodologies, and the reduction and reporting of data. The objective is to provide a uniform basis for subsampling, sample handling, instrument condition, methods control, performance evaluation, and analytical data generation and reporting.

The scope of the program is for all laboratory operations (from sample receipt, through analysis, to data reduction/reporting) applied to trace organics samples. The scope includes those audit procedures used to evaluate the application of the procedures defined within this QA/QC program.

CONTENTS

- Explain the cause of missing data.

- Demonstrate the validation of data each time they are recorded, calculated, or transcribed.

To accomplish these objectives, Standard Operating Procedures should address the major elements upon which the final quality of the contractors work depends. Generally, these include but are nor limited to:

1. Organization and personnel,

2. Facilities and equipment,

3. Analytical methodology,

4. Sample custody procedures,

5. Quality control, and

6. Data handling.

A comprehensive, well-written QA SOP will address each of these essentiel aspects of QA. In the followiog descriptions these six major areas have been divided into sub-elements, where applicable.

ORGANIZATION AND PERSONNEL

QA Policy and Objectives - Each organizatinn should have a written quality assurance policy that should be made known ro all orgaoisation personnel. Objectives should be esrablished to produce data that meer contract requirements in terms of completeness, precision, accuracy, representativeness, documentation, and comparability. The SOP should requirs the preparation of a specific QA plan for the analysis.

QA Organizarion - The orgaoisatioo and management of the QA fnoction should be described in the contractor's SOP. Reporring relationships and responsibiliries should be clearly defined. A QA Coordinator or Supervisor should be appoinred and his responsibilities established. A description of the QC peperwork flow should be available. There should be a clear designation of those who are authnrized to approve data and resulrs. Reaposibilities for taking corractive acrion should be assigned to appropriate management personnel.

Parsonnel training - It is highly desirable that there be a treining program for employees. This system should include motivation toward producing date of acceprable quality and should involve "practice work" by the new employee. The quality of thia work can be immediately verified and discussed by the supervisor, with appropriate corractive action taken.

Document Control and Revisions - The SOP should include a system for docnmenting:

SECTION II - GENERAL QA/QC CONSIDERATION

The contractor should have a written QA/QC SOP which describes the in-house procedures that he employs to guarantee, to the extent possible, the quality of all analysis activities. It should describe the quality assurance and the quality control procedures used during the analysis.

Each contractor should prepare his own SOPs to suit the needs of his organization as he has best determined. There is, however, a recommended comprehensive QA/QC SOP. A QA SOP should contain essential elements. These essential elements are described in this section. In addition, a checklist has been prepared to aid the EMSL-LV in reviewing the laboratory's QA program and to facilitate feedback to the contractor on the suitability of his program with respect to contract requirements.

ELEMENTS OF A QA/QC SOP

All routine laboratory tasks should have written QA/QC Standard Operating Procedures. Standard Operating Procedures should be detailed documents describing who does what, when, where, how, and why. They should be sufficiently complete and detailed to ensure:

- Data of known quality and integrity are generated.
- The minimum loss of data due to out-of-control conditions.

Standard Operating Procedures will be:

- Adequate to establish the traceability of standards, instrumentation, samples, and environmental data.
- Simple, so a user with basic education, experience and/or training can properly use them.
- Complete enough so the user follows the directions in a stepwise manner.
- Consistent with sound scientific principles.
- Consistent with current EPA regulations, guidelines, and contract requirements.
- Consistent with the instrument manufacturer's specific instruction manuals.

Standard Operating Procedures will also provide for documentation sufficiently complete to:

- Record the performance of all tasks and their results.

Feedback and corrective action - The SOP should specify the corrective action that is to be taken when an analytical or sampling error is discovered or the analytical system is determined to be out of control. The SQP should require documentation of the corrective action and notification of the analyst of the error and correct procednres.

SAMPLE CUSTODY

Sample custody is a part of any good laboratory or field operation. Where samples may be needed for legal purposes, "chain-of-custody" procedures, as defined in Exhibit F must be used. However, at a minimum, the following sample custody procedures should be addressed in the QA/QC SOP.

CHAIN-OF-CUSTODY IN LABORATORY OPERATIONS

- Identification of responsible party to act as sample custodian at the laboratory facility authorized to sign for incoming field samples, obtain documents of shipment (e.g., bill of lading number or mail receipt), and verify the data entered onto the sample custody records.

- Provision for a laboratory sample custody log consisting of serially numbered standard lab-tracking report sheets.

- Specification of laboratory sample custody procedures for sample handling, storege and dispersement for analysis.

QUALITY CONTROL

Quality Control Procedures - The quality control procedures used during analysis should be described and must conform to those described in Exhibit E. The quality control checks routinely performed during sample analysis include reagent blank analysis to establish analyte levels, duplicate analysis to establish analytical precision, spiked and blank sample analysis to determine analytical accuracy. The frequency of these quality assurance checks are defined in the contract. Limits of acceptance or rejection are also defined for analysis and control charts should be used. Confirmation procedures should be described in the SOP.

Control Checks and Internal Audits - A good SOP will make provision for and describe control checks and internal audits by the contractor. Several approaches are used for control checks. These include:

1. Reference material analysis. Analytical reference materials are available from several commercial and government sources, or they may be prepared in-house. The chemical analysis of these materials has been well established. Such materials can be analyzed along side routine samples and the results used to check the accuracy of analytical procedures.

2. Blank analysis. The procedures and the frequency of blank analyses are defined in the contract.

1. Calibration procedures,

2. Analytical procedures,

3. Computational procedures,

4. Quality control procedures,

5. Bench data,

6. Operating procedures, or any changes to these procedures, and

7. Laboratory notebook policy.

Procedures for making revisions to rechnical procedure or documents must be clearly defined, with the lines of authority indicated. Procedural revisions should be written and distributed to all affected individuals, thns ensuring implementation of changes.

FACILITIES AND EQUIPMENT

Prncurement and Tnventory Procaduras - Purchasing guidelines for all equipment and reagents having ao effect on data quality should be well-defined aod documented. Similarly, performance specifications should be documented for all items of equipment baving an effect on data quality. Once any item which is critical to the anelysis such as an in situ instrument, or reagent is received and accepted by the organization, documentation should be retained of the type, age, and acceptance stetus of the item. Reagents should be dated upon receipt in order to establish their order of use and to minimize the possihility of exceeding their useful shelf life.

Preventive Maintanance - Preventive maintenance procedures should be clearly defined and written for each measurement system and raquired support aquipment. When maintenance activity is necessary, it should be documented on standerd forms maintained in logbooks. A history of the maintenance record of each system serves as an indication of the adequacy of maintenance schedules and parts invenrory.

ANALYTICAL METHODOLOGY

Calibration and Operating Procedures - Calibration is the process of establishing the relationship of a measurement system output to a known stimulus. In essence, calihration is a raproducible reference point to which all sample measurements can be correlated. A sound calibration SOP should include provisions for documentation of fraquency, conditions, standerds, and records reflecting the calibration history of a measurement system.

The accurecy of the calibration standards is an important point to consider since all data will be in reference to the standards used. An SOP for verifying the accuracy of all working standerds against primary grade standards should be routinely followed.

SECTION III - QA/QC REQUIREMENTS

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

- Documentation of GC/MS Mass Calibration and Abundance Pattern
- Documentation of GC/MS Response Factor Stability
- Internal Standard Response and Retention Time Monitoring
- Reagent Blank Analysis
- Surrogate Spike Response Monitoring
- Matrix Spike and Matrix Spike Duplicate Analysis
- Specific QA/QC for Pesticide Analysis

Part 1 Tuning and GC/MS Mass Calibration

1.0 SUMMARY

Prior to initiating any on-going data collection, it is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria. This is accomplished through the analysis of Decafluorotriphenylphosphine (DFTPP) or p-Bromofluorobenzene (BFB). The ion abundance criteria for each calibration compound MUST be met before any samples, blanks or standards can be analyzed.

1.1 Decaflunrotriphenylphosphine (DFTPP)

Each GC/MS system used for the analysis of semi-volatile or pesticide HSL compounds must be hardware tuned to meet the abundance criteria listed in Table 1.1 for a 50 ng injection of decaflunrotriphenylphosphine (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 more frequent. DFTPP must he injected to meet this criterion. Background subtraction should 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 contrary to the objectives of Quality Assurance and are unacceptable.

1.2 Documentation

Documentation of the calibration must be provided in the form of a bar graph plot and as a mass listing. (See examples in Figures 1.1 and 1.2.) (Use of specific manufactnrer's instrumentation and data output for example(s) does oot imply any andnraement by the USEPA.)

3. Matrix spike analysis. The procednres and the frequency of matrix spike anulyaas are defined in the contract.

4. Duplicete snalysis. The procedures sod the frequency nf duplicate snalyaes sre defined in the contract.

5. Internal sudits. laternal sudits should be periodically conducted to evaluate the functioning of the QA SOP. This involves an independent check of the performance of the laboratory snalysts to determine if prescribed procedures sre closely followed.

DATA HANDLING

Data Handling, Reporting, snd Recordkeeping - Data hendling, reporting, snd recnrdkeaping procedures shnuld ba described. Data hendling snd reporting inclndes all procedures usad to racord data on standard forms, snd in laboratory notebooks. The reporting format for differeot types of bench deta should be described snd the forms provided. The contents of notebooks should be specified.

Recordkeeping of this type servas at least two useful fnnctions: (1) it makes possible the reanalysis of a set of data at a future time, snd (2) it may be used in support of the axperimenral conclusions if varions sapecca of the snalysis sre called into question.

Dara Validarion - Dara validation procedures, defined ideally ss a set of computerized snd manual checks applied at various appropriate levels of the measurement process, should be in written form snd clearly defined for all measuremant systems. Criteria for data validation must be documeoted snd include limits oo: (1) operational parameters such as GC conditions; (2) calibration data; (3) special checks unique to sach measuramant, s.g., succesaive values/averagas; (4) statisrical tesrs, e.g., outliers; snd (5) manual checks such as hand calculatinns. The limits defined in the contract ansure a high probability of detecting invalid data for either all or the majnrity of the meesuramant systems. The raquired data validation activities (GC operating conditions, snalytical precision, atc.) should be recorded on standard forms in a logbook.

LABORATORY EVALUATION CHECKSHEETS

An important responsibility of the EMSL-LV is to review the QA SOP of the conrractor before work begins. A checklist has been provided in Exhibit E to assist tha EMSL-LV io reviewing a contractor's QA program. In the event a contractor doas nnt have a written QA program, this checklist may srill be used to svaluats the QA procedues employed or to assist the contractor to devalop a suitable QA SOP.

MASS LIST DATA: B4DFTPP012 # 347 BASE M/E:
01/20/84 8:03.00 # 8:47 CAL1: B4FC430120 # 4 RIC: B19648
SAMPLE: 50 NG DFTPP
6336 TO 6358 BUMPED - 6330 TO 6335 SMO Case: 0000

46 / 349 MASS		% BA	% RIC	0. / 0 INTEN.	MINIMA / MAXIMA MASS	MIN INTEN:	% BA	% RIC	838. INTEN.
50.00	B	12.91	1.92	9328.	175.00		2.07	0.24	937.
51.00	B	51.42	6.08	13360.	177.00		0.93	0.11	241.
52.00		3.78	0.45	982.	179.00	B	4.06	0.48	1054.
55.00		1.28	0.15	333.	180.00	B	2.32	0.27	604.
57.00	B	3.84	0.45	999.	181.00	B	1.23	0.15	319.
63.00	B	8.39	0.28	621.	185.00		8.00	0.24	919.
65.00		1.19	0.14	309.	186.00		13.69	1.62	3556.
69.00	B	44.70	5.29	11616.	187.00	B	4.38	0.52	1138.
73.00	B	3.01	0.36	783.	191.00	B	1.29	0.15	336.
74.00		4.93	0.58	1280.	192.00		1.09	0.13	283.
75.00	B	6.67	0.79	1734.	193.00		8.11	0.23	849.
76.00		2.71	0.32	703.	196.00		2.54	0.30	660.
77.00	B	48.28	8.71	12544.	198.00		100.00	11.83	25984.
78.00	B	2.82	0.33	733.	199.00		7.38	0.87	1918.
79.00		3.86	0.30	666.	204.00		4.04	0.48	1050.
80.00		5.32	0.27	602.	205.00	B	5.92	0.70	1538.
81.00		4.11	0.49	1068.	206.00		23.37	2.76	6072.
83.00	B	0.99	0.12	257.	207.00	B	3.78	0.45	981.
85.00	B	1.33	0.16	346.	208.00	B	1.62	0.19	422.
88.00		1.12	0.13	290.	217.00		7.82	0.89	1954.
93.00	B	4.66	0.55	1812.	221.00	B	5.22	0.62	1356.
96.00		1.79	0.21	465.	222.00		1.06	0.13	276.
98.00	B	3.01	0.36	781.	223.00	B	1.14	0.13	295.
99.00	B	2.52	0.30	655.	224.00		13.32	1.60	2312.
101.00		1.95	0.23	506.	225.00	B	3.14	0.37	817.
104.00		1.43	0.17	372.	227.00		5.67	0.67	1474.
105.00	B	1.24	0.15	322.	231.00		1.02	0.12	264.
107.00	B	14.04	1.66	3648.	244.00		10.07	1.19	2616.
108.00		2.59	0.31	672.	245.00		1.42	0.17	370.
110.00		22.23	2.63	5776.	246.00	B	1.22	0.14	317.
111.00		3.94	0.47	1023.	255.00		45.57	5.39	11840.
117.00	B	10.34	1.23	2740.	256.00		6.67	0.79	1732.
123.00		1.60	0.19	416.	258.00		3.56	0.42	924.
127.00		47.78	5.65	12416.	265.00		1.39	0.16	360.
128.00		3.68	0.44	956.	273.00	B	1.58	0.19	411.
129.00	B	17.09	3.02	4440.	274.00		3.51	0.41	911.
130.00		2.04	0.24	530.	275.00		23.12	2.74	6008.
135.00	B	1.92	0.23	499.	276.00		3.02	0.36	784.
136.00		1.05	0.12	273.	277.00		2.07	0.24	537.
141.00		2.02	0.24	524.	281.00	B	2.07	0.24	537.
148.00		2.90	0.34	753.	296.00		6.89	0.81	1790.
149.00	B	1.33	0.16	345.	297.00		0.99	0.12	258.
155.00		1.90	0.22	494.	323.00		2.47	0.29	641.
156.00		2.31	0.27	599.	334.00		1.72	0.20	448.
161.00		1.31	0.15	340.	352.00		1.00	0.12	259.
165.00		1.13	0.13	291.	365.00		3.57	0.42	927.
167.00		5.23	0.62	1360.	423.00	B	3.35	0.40	870.
168.00		3.46	0.41	898.	441.00		11.61	1.37	3016.
169.00	B	1.22	0.14	316.	442.00		61.82	7.31	16064.
174.00		0.92	0.11	238.	443.00		11.93	1.41	3100.

Figure 1.1b. Mass listing DFTPP (Finnigan).

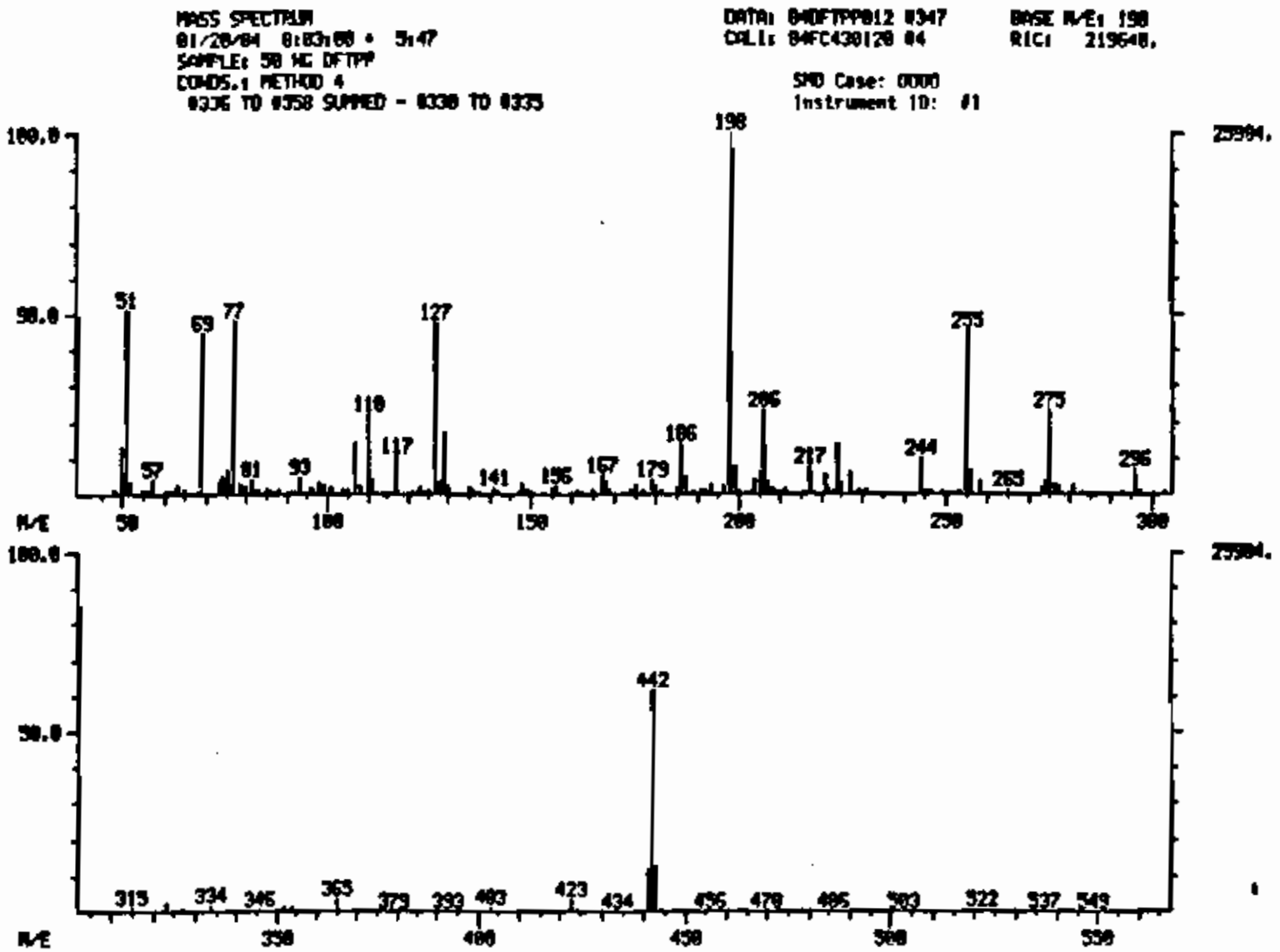


Figure 1.1a. DFTPP bar graph output (Finnigan).

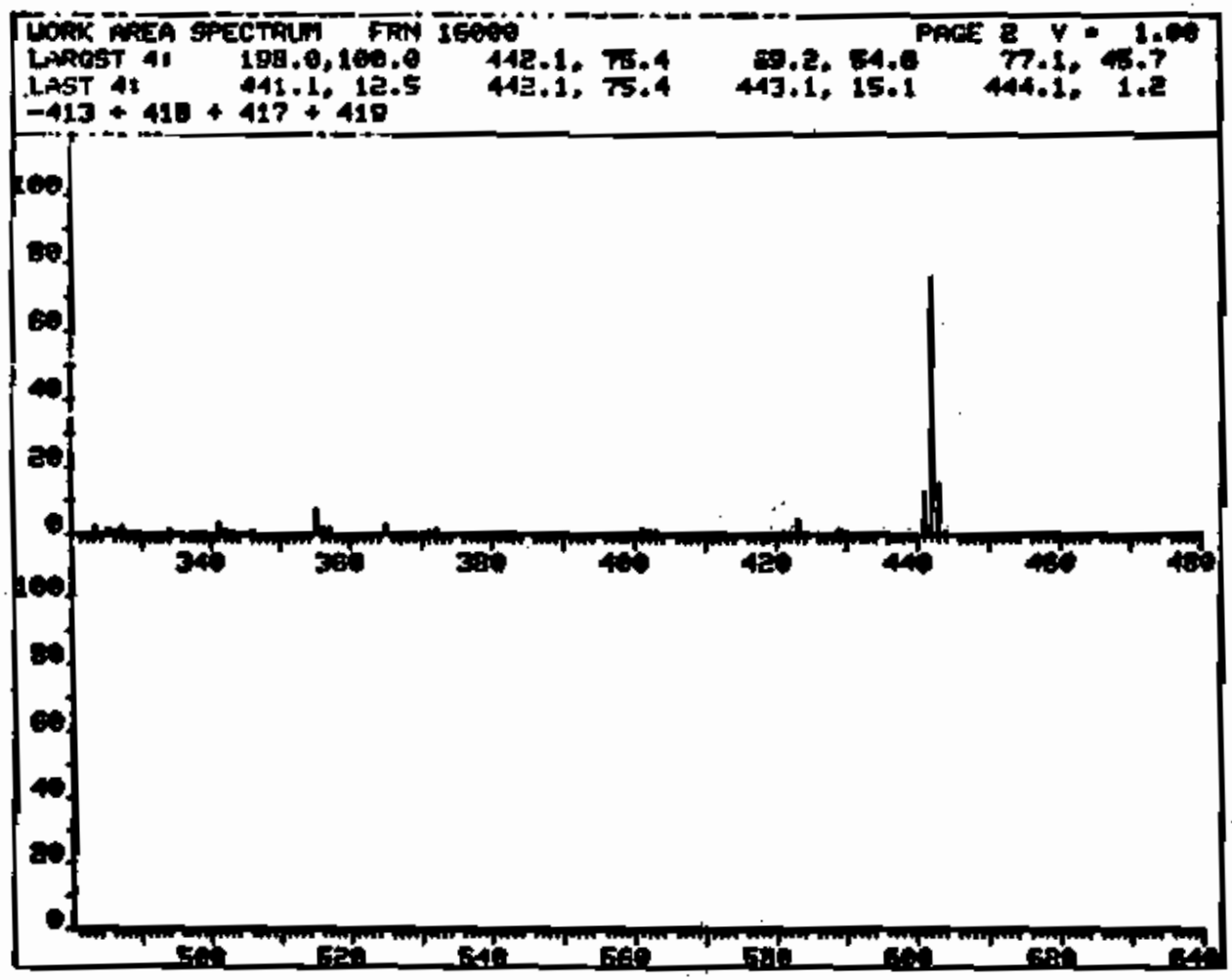


Figure 1.2b. Mass listing DFTPP (Hewlett Packard).

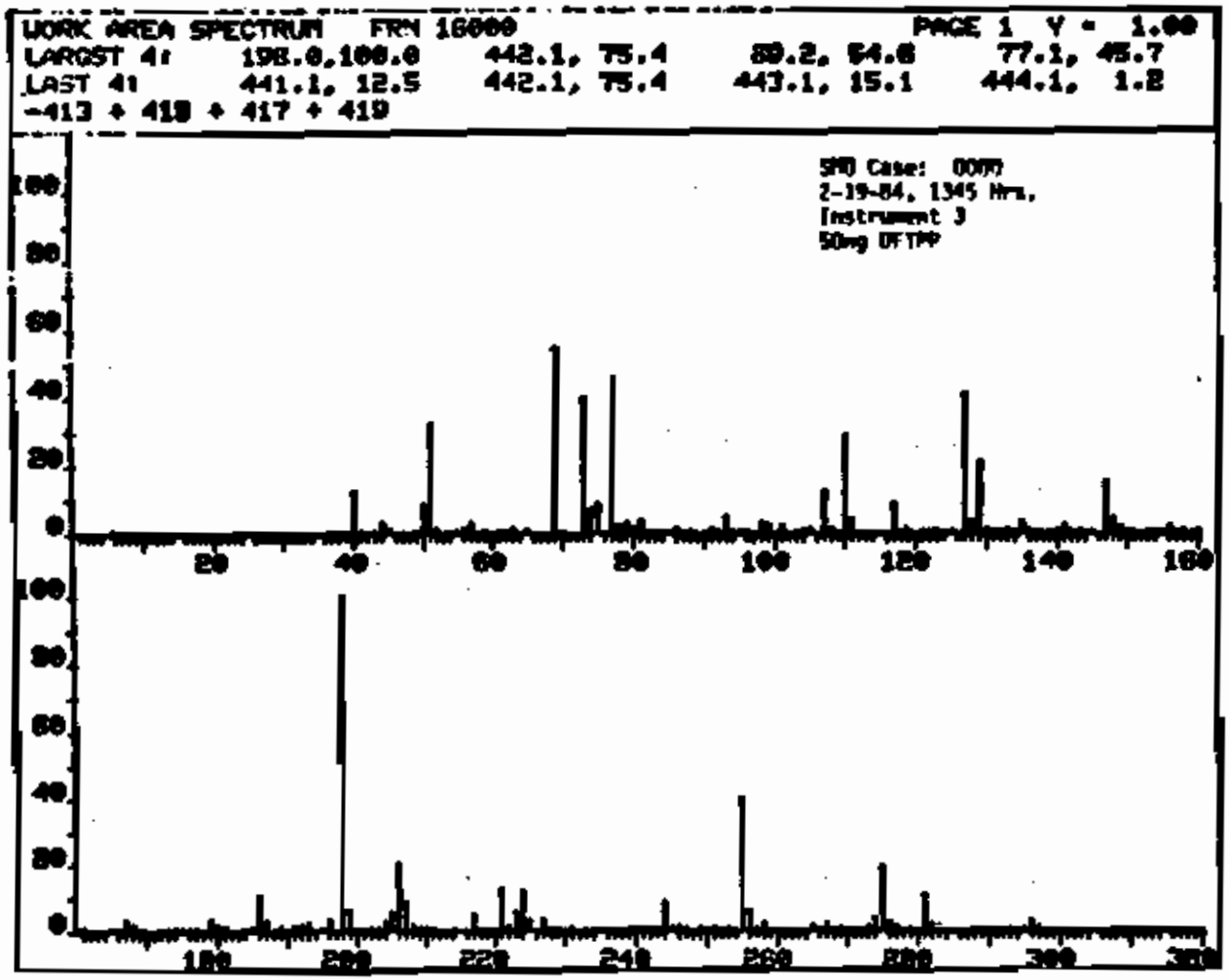


Figure 1.2a. DFTPP bar graph output (Hewlett Packard).

WORK AREA FRM 16000 —413 + 418 + 417 + 413
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
176	.7	208	1.2	251	.6	296	8.8
177	.7	209	1.2	253	.3	297	1.2
179	3.3	210	.4	255	40.1		
180	2.0	211	.6	256	5.9	303	.4
181	1.3			257	.4		
184	.3	217	4.8			314	.3
185	1.4	218	.3	258	8.3	315	.4
186	10.5	221	12.6	265	1.8	323	8.1
187	3.0	222	1.5	266	.7	325	1.4
		223	5.8	267	8.3	326	.8
189	1.0	224	12.0	268	.7	327	8.4
191	1.3	225	3.3	269	.0		
192	1.5	227	3.4			338	.7
193	8.8	228	.4	273	1.6	329	.8
195	.3	229	.9	274	4.1	334	1.6
196	3.3			275	19.2	341	8.8
198	100.0	231	.3	276	2.8		
199	8.4	237	.4	277	1.6	348	1.1
200	.3	241	.3	279	.3	343	.9
202	.5	242	.4	281	10.8	348	.3
		243	.5	282	2.4	352	.4
203	.3			283	1.6	353	.4
203	.4	244	8.4	284	.3	354	.4
204	2.7	245	1.2			355	7.1
205	5.4	246	1.3	293	.3		
206	88.0	247	.3	295	.2	356	8.1
207	8.4	249	1.1	296	2.8	357	1.7
						(CONT)	

Figure 1.2b. (Continued).

SMD Case: DMD
2-19-84, 1345 Hrs.

Instrument 3
50mg DFTPP

WORK AREA FRM 15000 -413 + 418 + 417 + 419
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
40	18.3	78	2.7	110	28.4	143	.4
41	.3	79	3.8	111	4.2	145	.4
43	.3	80	2.0	112	.4		
44	2.9	81	3.0	117	8.6	147	15.1
46	1.4	82	.8			148	4.4
		83	.5	118	.8	149	2.1
49	.1	84	.7	119	.3	150	.3
50	8.7	85	.8	122	.6	151	.8
51	31.7	86	1.5	123	1.0	153	.5
52	1.5	87	.8	124	.6	154	.4
55	.4	88	.4	125	.5	155	.0
56	1.3			127	41.2	156	1.9
57	3.0	91	1.8	128	3.0	157	.4
59	.8	92	.0	129	21.1	158	.3
61	.4	93	4.8	130	1.8		
		94	.3	131	.4	160	.8
62	.5	95	.3	131	.7	161	1.1
63	1.8	96	.8			165	.0
65	1.1	98	3.0	132	.3	168	.5
69	54.8	99	8.7	133	1.8	167	3.5
70	.3	101	8.8	134	.8	168	1.8
73	30.8	103	.9	135	3.3	169	.3
74	7.8			136	.6	172	.3
75	9.0	104	1.0	137	.8	173	.4
		105	1.4	140	.3		
76	.8	107	18.8	141	8.8	174	.7
77	46.7	108	1.7	140	.7	175	.0
						<CONT>	

Figure 1.2b. (Continued).

1.2.1 The laboratory is required to 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 on the bottom of the appropriate Form V. Detailed instructions for the completion of Form V are found in Exhibit B, Section III.

TABLE 1.1. 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

1.3 p-Bromofluorobenzene (BFB)

Each GC/MS system used for the analysis of volatile HSL compounds must be hardware tuned to meet the abundance criteria listed in Teble 1.2 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, Section IV. This criterion must be demonstrated daily or for each twelve (12) hour time period, whichever is more frequent. Background subtraction should he 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 contrary to the objectives of Quality Assurance and are unacceptable.

1.4 Documentation

Documentation of the calibration must be provided in the form of a bar graph plot and as a mass listing. (See examples in Figures 1.3 and 1.4.)

1.4.1 The laboratory is required to complete a Form V (GC/MS Tuning and Mass Calibration) <u>each time</u> 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 on the bottom of the appropriate Form V. Detailed instructions for the completion of Form V are found in Exhibit B, Section III.

```
WORK AREA FRM 16000  -413 + 418 + 417 + 419

MASS    ABUND

365       2.5

371         .4
372        1.3
373         .4
383         .3

385         .3

401        1.4
402        1.1
403        1.1

415         .8
421         .5
422         .5
423        4.3
424         .7

429        1.5
430         .6

441       18.5
442       75.4
443       16.1
444        1.8
>PAUSE
```

Figure 1.2b. (Continued).

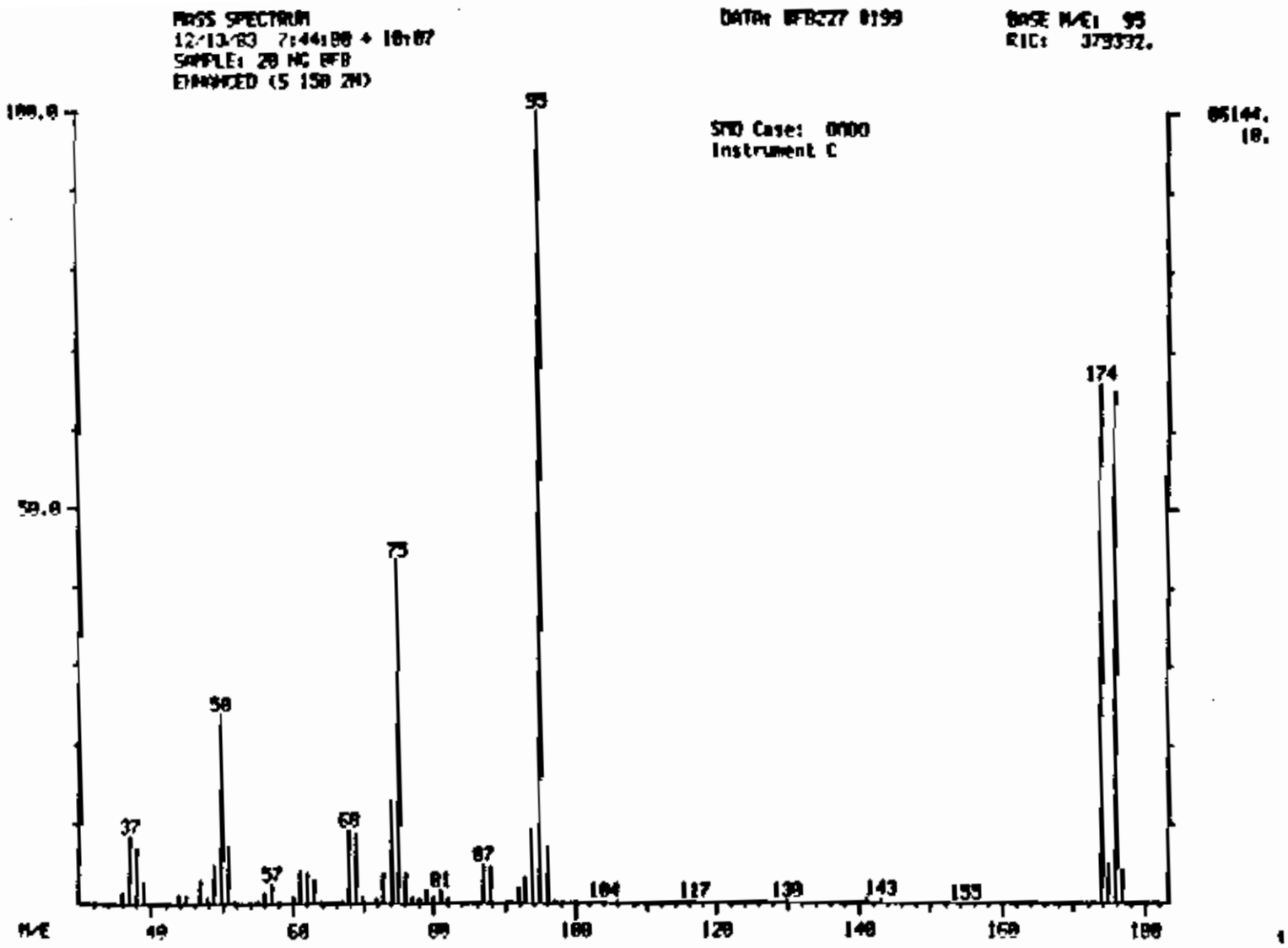


Figure 1.3a. BFB bar graph (Finnigan).

TABLE 1.2. 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 1.00 percent of the base peak
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

NOTE: Whenever the Laboratory takes corrective action which may change or affect the tuning criteria for DFTPP or BFB (e.g., ion source cleaning or repair, etc.), the tune must be verified irrespective of the 12-hour tuning requirements.

DFTPP and BFB criteria MUST be met before any samples, sample extracts, blanks or standards are analyzed. Any samples analyzed when tuning criteria have not been met may require reanalysis at no cost to the Agency.

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 or BFB analysis that the laboratory submits as documentation of compliant tune. The time period ends after twelve (12) hours has elapsed according to the system clock.

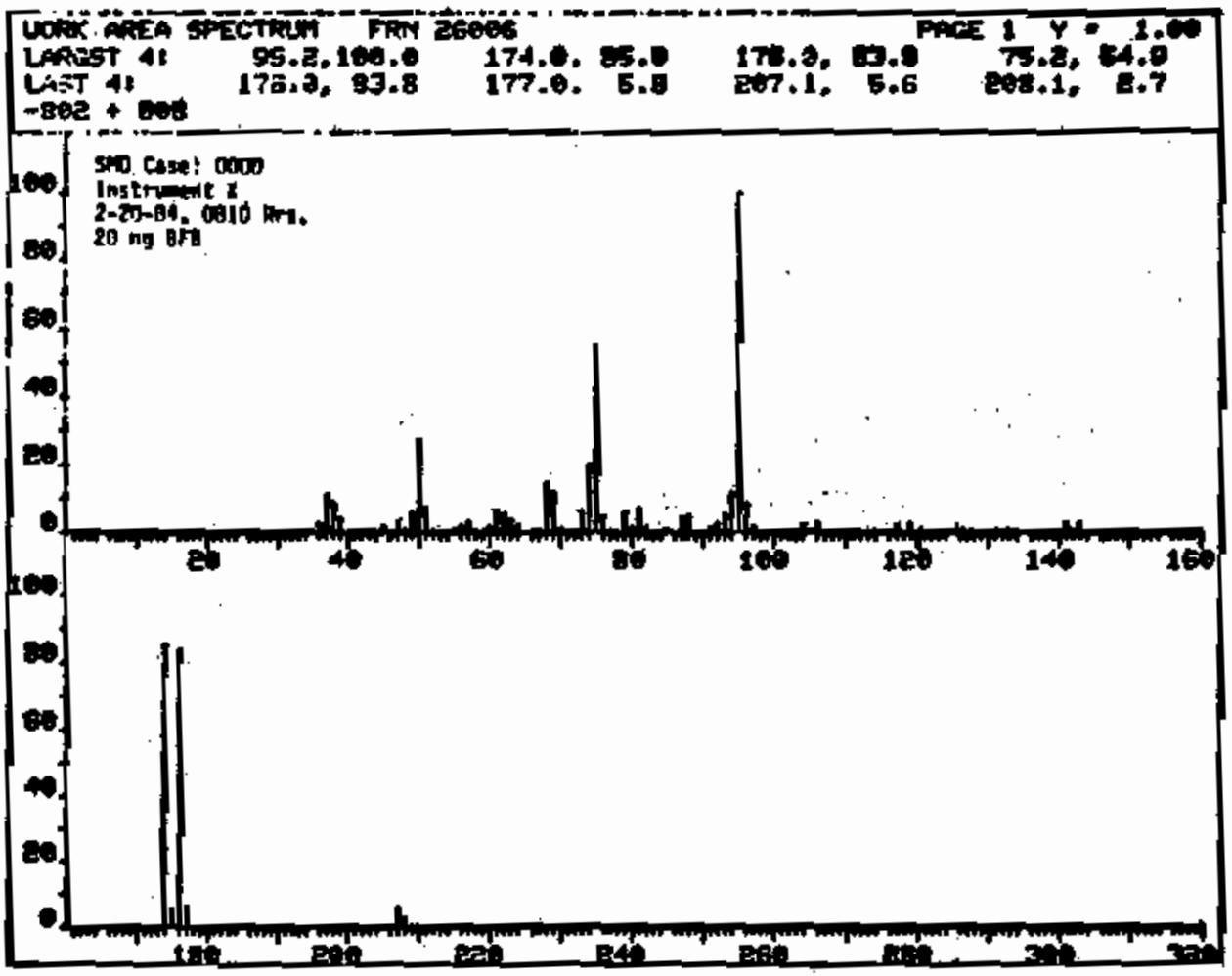


Figure 1.4a. HPB bar graph (Hewlett Packard).

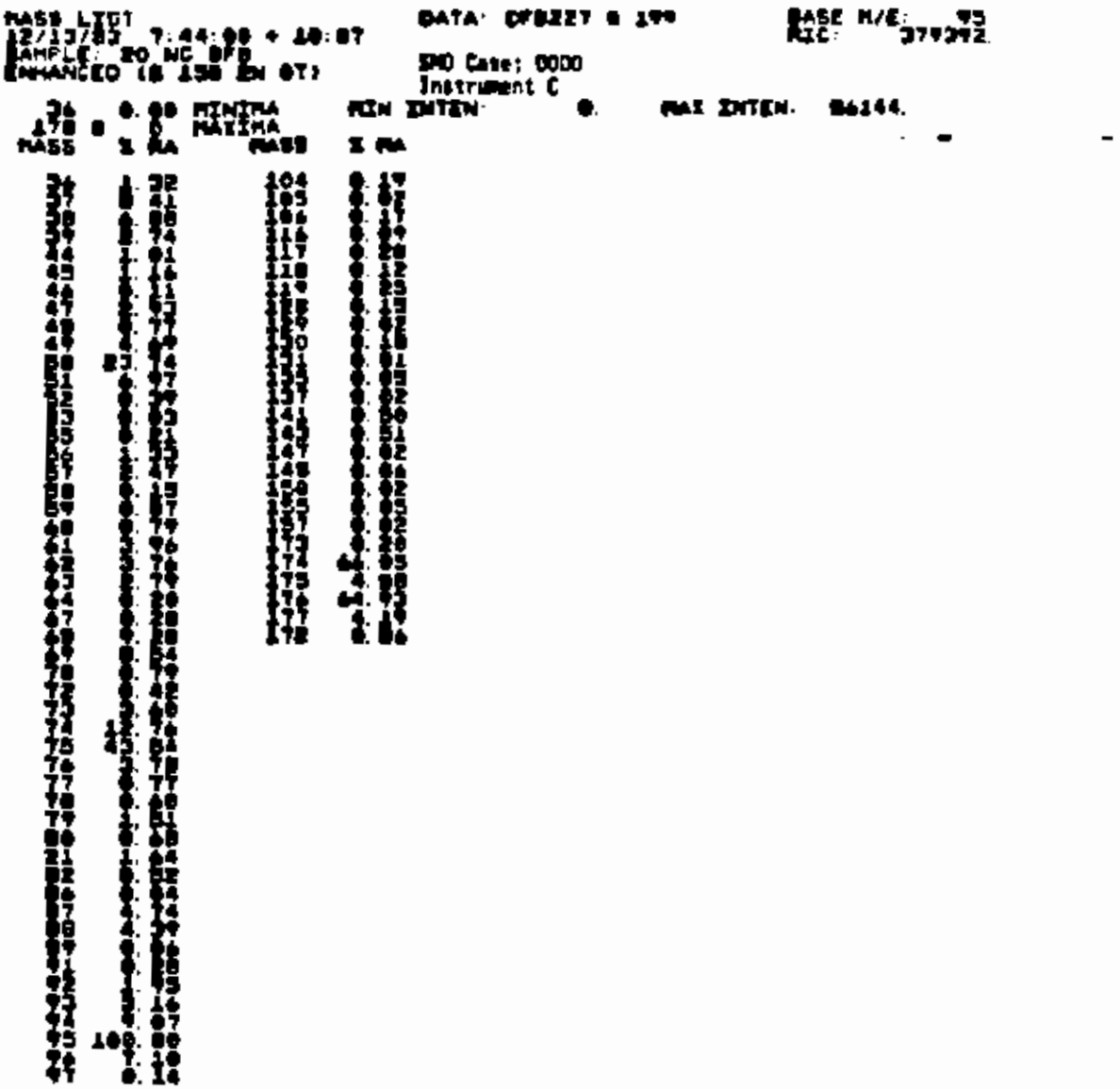


Figure 1.3b. Mass listing BFB (Finnigan).

Part 2. Calibration of the GC/MS System

2.0 SUMMARY

Prior to the analysis of samples 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 HSL compound standards. For GC/MS analysis, typical linear ranges are 0-400 ng for base neutrals, 0-1000 ng for phenols and 0-1000 ng for volatiles. 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, Section IV, to yield the following specific concentrations:

2.1.1 Volatile HSL Compounds

Initial calibration of volatile HSL compounds is required at 20, 50, 100, 150 and 200 ug/L. Utilizing the analytical protocol specified in Exhibit D this will result in 100-1000 total ng analyzed. If a sample 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 on Form VI and in the Case Narrative, and proceed with a four-point initial calibration for that specific analyte.

2.1.2 Semi-volatile and Pesticide HSL Compounds

Initial calibration of semi-volatile HSL compounds is required at 20, 50, 80, 120, and 160 total nanograms. 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. Benzidine only requires a three-point calibration at 80, 120 and 160 total nanograms, since detection is not required below 80 nanograms per injection (80 ug/L).

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. Establishment of standard calibration procedures is necessary and deviations by Contractor Laboratories will not be allowed.

2.3 Analyze each calibration standard and tabulate the area of the primary characteristic ion (Exhibit D, Table 4 and Table 5) 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 except for N-nitrosodimethylamine. Late eluting compounds usually will have much better agreement. N-nitrosodimethylamine MUST be resolved from the solvent.

WORK AREA FRN 25008 -882 + 888

MASS	ABUND	MASS	ABUND	MASS	ABUND
36	2.6	73	8.1	141	2.8
37	10.5	74	80.0	143	2.8
38	2.7	76	54.9		
39	4.8			174	95.0
45	1.8	76	4.7	175	5.4
47	3.1	77	.8	176	83.8
		79	5.7	177	15.8
48	.7	80	1.8		
49	5.8	81	6.7	887	5.8
50	27.1	82	1.8	888	6.7
51	7.8	87	4.1	>PAUSE	
52	.1	88	4.8		
55	.8				
56	1.8	91	.4		
57	2.8	92	8.6		
58	.8	93	5.1		
60	1.7	94	11.4		
61	8.3	95	100.0		
		96	8.4		
62	5.4	97	8.0		
63	3.8				
64	8.0	104	6.8		
67	.3	105	.8		
68	14.4	106	8.8		
69	11.8	117	8.1		
70	1.1				
76	.8	119	8.7		

SMD Case: 0000 -
Instrument X
2-20-84, 0810 Hrs
20ng BFB

Figure 1.4b. Mass listing BFB (Hewlett Packard).

2.4.1 For volatiles, the five System Performance Check Compounds (5PCC's) are: chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane and chlorobenzene. The minimum acceptable average response factor ($\overline{RF}$) for these compounds is 0.300. These compounds typically have RF's 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. Examples of these occurrences are:

TABLE 2.1. VOLATILE INTERNAL STANDARDS WITH CORRESPONDING HSL ANALYTES ASSIGNED FOR QUANTITATION

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

(surr) = surrogate compound

- Chloromethane - this compound is the most likely compound to be lost if the purge flow is too fast.

- 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 effected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

- 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 For semivolatiles, the System Performance Check Compounds (SPCC's) are: N-Nitroso-Di-n-Propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol and 4-Nitrophenol. The minimum acceptable average response factor ($\overline{RF}$) for these compounds is 0.050. These compounds (SPCC's) typically have very low

Using Table 2.1 and Table 2.2, calculate the response factors (RF) for each compound at each concentration level using Equation 2.1.

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

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 3.3 or 3.4.

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 response factors (RF) from the initial calibration, calculate the percent relative standard deviations (%RSD) for compounds labeled as Calibration Check Compounds 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 5 response factors (per compound)

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

$\bar{x}$ = mean of initial 5 response factors (per compound)

The %RSD for each individual Calibration Check Compound must be <u>less</u> than 30 percent. This criteria must be met for the inirial calibration to be valid.

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

RF's (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.

2.4.3 The initial calibration is valid only after both the %RSD for CCC compounds and the minimum $\overline{RF}$ 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 response factor ($\overline{RF}$) and percent relative standard deviation (%RSD) for all HSL compounds. The laboratory is required to submit a Form VI (Initial Calibration Data) for each instrument used to analyze samples under this IBF protocol. Detailed instructions for completion of Form VI are found in Exhibit B, Section III.

2.6 Continuing Calibration

A calibration standard(s) containing all volatile or semi-volatile HSL compounds, including all required surrogates, must be performed each twelve (12) hours during analysis. Compare the response factor data from the standards each twelve hours with the average response factor from the initial calibration for a specific instrument. A system performance check must be made each twelve hours. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration (Form VI). If the minimum 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 response factor (RF) for semivoletile System Performance Check Compounds (SPCC) is 0.050. The minimum response factor (RF) for volatile System Performance Check Compounds (SPCC) is 0.300.

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.

$$\% \text{ Difference} = \frac{\overline{RF_I} - RF_c}{\overline{RF_I}} \times 100 \qquad \text{Eq. 2.3}$$

where

$\overline{RF_I}$ = average response factor from initial calibration.

RF_c = response factor from current verification check standard.

TABLE 2.2. SEMI-VOLATILE INTERNAL STANDARDS WITH CORRESPONDING HSL ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}	Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
N-Nitrosodimethylamine	Nitrobenzene	Hexachlorocyclopentadiene	4,6-Dinitro-2-methylphenol	Benzidine	Di-n-octyl Phthalate
Phenol	Isophorone	2,4,6-Trichlorophenol	N-nitrosodiphenylamine	Pyrene	Benzo(b)fluoranthene
Aniline	2-Nitrophenol	2,4,5-Trichlorophenol	1,2-Diphenylhydrazine	Butylbenzyl Phthalate	Benzo(k)fluoranthene
bis(2-Chloroethyl) ether	2,4-Dimethylphenol	2-Chloronaphthalene	4-Bromophenyl Phenyl Ether	3,3'-Dichlorobenzidine	Benzo(a)pyrene
2-Chlorophenol	Benzoic acid	2-Nitroaniline	Hexachlorobenzene	Benzo(a)anthracene	Indeno(1,2,3-cd) pyrene
1,3-Dichlorobenzene	bis(2-Chloroethoxy)methane	Dimethyl Phthalate	Pentachlorophenol	bis(2-ethylhexyl) Phthalate	Dibenz(a,h) anthracene
1,4-Dichlorobenzene	2,4-Dichlorophenol	Acenaphthylene	Phenanthrene	Chrysene	Benzo(g,h,i) perylene
Benzyl Alcohol	1,2,4-Trichlorobenzene	3-Nitroaniline	Anthracene	Terphenyl-d_{14} (surr)	
1,2-Dichlorobenzene	Naphthalene	Acenaphthene	Di-n-butyl Phthalate		
2-Methylphenol	4-Chloroaniline	2,4-Dinitrophenol	Fluoranthene		
bis(2-Chloroisopropyl)ether	Hexachlorobutadiene	4-Nitrophenol			
4-Methylphenol	4-Chloro-3-methylphenol	Dibenzofuran			
N-nitroso-Di-n-propylamine	2-Methylnaphthalene	2,4-Dinitrotoluene			
Hexachloroethane	Nitrobenzene-d_5 (surr)	2,6-Dinitrotoluene			
2-Fluorophenol (surr)		Diethyl Phthalate			
Phenol-d_6 (surr)		4-Chlorophenyl-phenyl ether			
		Fluorene			
		4-Nitroaniline			
		2-Fluorobiphenyl (surr)			
		2,4,6-Tribromo Phenol (surr)			

Surr = surrogate compound

Part 3 Reagent Blank Analysis

3.0 SUMMARY

A reagent blank is a volume of deionized, distilled laboratory water for water samples, or a purified solid matrix (supplied by EMSL-LV[1]) for soil/sediment samples carried through the entire analytical scheme (extraction, concentration, and analysis). The reagent blank volume or weight must be approximately equal to the sample volumes or sample weights being processed.

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

3.1.1 For the analysis of volatile HSL compounds, a reagent blank analysis must be performed every twelve hours, once per Case[2] or with every twenty (20) samples of similar concentration and/or sample matrix, whichever is more frequent, on each GC/MS system used to analyze samples.

3.1.2 For the analysis of semi-volatile or pesticide HSL compounds, a reagent blank analysis must be performed once each Case[2], with every twenty (20) samples of similar concentration and/or sample matrix or whenever samples are extracted by the same procedure (separatory funnel or continuous extraction), whichever is more frequent. The reagent blank associated with a specific set or group of samples must be analyzed on each GC/MS or GC system used to analyze that specific group or set of samples.

3.2 It is the laboratory'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 reagent blank should meet the criteria of paragraphs 3.2.1.1, 3.2.1.2, and 3.2.1.3.

3.2.1.1 A reagent blank for volatile analysis should contain no greater than two times (2X) the Contract Required Detection Limit (CRDL from Exhibit C) of common laboratory solvents (common laboratory solvents are: methylene chloride, acetone, and toluene). The reagent blank must not contain greater than five times (5X) the CRDL of those compounds previously listed.

3.2.1.2 A reagent blank for semi-volatile analysis should contain no greater than two times (2X) the Contract Required Detection Limit (CRDL from Exhibit C) of common phthalate esters. The reagent blank must not contain greater than five times (5X) the CRDL of any phthalate ester.

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[1] EPA EMSL-Las Vegas is studying the feasibility of providing a solid matrix to each contractor, at no charge, to be used as reagent blank material.

[2] A Case is a group or a set of samples collected from a particular site over a given period of time.

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 25%, the initial calibration is assumed to be valid. If the criteria are not met (>25% 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. This criteria MUST be met before sample analysis begins.

TABLE 2.3. CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction	Volatile Fraction
Acenaphthene	4-Chloro-3-Methylphenol	1,1-Dichloroethene
1,4-Dichlorobenzene	2,4-Dichlorophenol	Chloroform
Hexachlorobutadiene	2-Nitrophenol	1,2-Dichloropropane
N-Nitroso-di-n-phenylamine	Phenol	Toluene
Di-n-octylphthalate	Pentachlorophenol	Ethylbenzene
Fluoranthene	2,4,6-Trichlorophenol	Vinyl Chloride
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 volatile HSL compound in the continuing calibration standard(s) is 50 ug/L.

2.6.3.2 The concentration for each semi-volatile HSL compound in the continuing calibration standard(s) is 50 total nanograms. Ten compounds: Benzoic Acid, 2,4-Dinitrophenol, 2,4,5-Trichlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, 4,6-Dinitro-2-methylphenol, Pentachlorophenol and Benzidine will be analyzed at 80 total nanograms of each compound injected.

2.7 Documentation

The laboratory is required to complete and submit a Form VII for each GC/MS system utilized for each twelve hour time period. Calculate and report the response factor and percent difference (%D) for all compounds. Ensure the minimum RF for volatile SPCC's is 0.300 and for semivolatile SPCC's is 0.050. The percent difference (%D) for each CCC compound must be less than 25 percent. Additional instructions for completing Form VII are found in Exhibit B, Deliverables, Section III.

taken before further sample analysis proceeds. All samples processed with a reagent blank that is out of control (i.e., contaminated) must be reextracted/repurged and reanalyzed at no additional cost to the Agency. The Laboratory Manager, or his designate, must address problems and solutions in the Case narrative (Exhibit B).

3.3 Documentation

Results of reagent blank analysis shall be reported using the Organic Analysis Data Sheet (Form I) signed in original signature by the laboratory manager or his designate, and the tentatively identified compounds (Form I, Part B). In addition, the results from reagent blanks must be summarized on Form IV (Reagent Blank Summary). Specific instructions for the completion of these forms can be found in Exhibit B (Reporting and Deliverables), Section III.

3.3.1 The Contractor will report ALL sample concentration data as UNCORRECTED for blanks. It shall be the responsibility of the EPA evaluator, and/or data auditor, to correct analyte concentrations for concentrations detected in the reagent blank(s). It is the Contractor's responsibility to ensure the proper number of reagent blanks are analyzed and the data properly reported.

Part 4 Surrogate Spike (SS) Analysis

4.0 SUMMARY

4.1 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.

4.2 Each sample (including matrix spike and matrix spike duplicate) and blank are spiked with surrogate compounds prior to purging or extraction. The surrogate spiking compounds shown in Table 4.1 are used to fortify each sample or blank with the proper concentrations. Performance based criteria are generated from laboratory results. Therefore deviations from spiking protocol will not be permitted.

TABLE 4.1. SURROGATE SPIKING COMPOUNDS

Compound	Fraction	Amount in Sample Extract* (before any optional dilutions) Low H_2O	Medium H_2O	Low Soil	Medium Soil
Toluene-d_8	VOA	50 ug	50 ug	50 ug	50 ug
4-Bromofluorobenzene	VOA	50 ug	50 ug	50 ug	50 ug
1,2-Dichloroethane-d_4	VOA	50 ug	50 ug	50 ug	50 ug
Nitrobenzene-d_5	BNA	50 ug	50 ug	50 ug	50 ug
2-Fluorobiphenyl	BNA	50 ug	50 ug	50 ug	50 ug
p-Terphenyl-d_{14}	BNA	50 ug	50 ug	50 ug	50 ug
Phenol-d_5	BNA	100 ug	100 ug	100 ug	100 ug
2-Fluorophenol	BNA	100 ug	100 ug	100 ug	100 ug
2,4,6-Tribromophenol	BNA	100 ug	100 ug	100 ug	100 ug
Dibutylchlorendate	Pest.	0.1 ug	0.1 ug	0.1 ug	0.1 ug

* at the time of injection

3.2.1.3 For all other HSL compounds not listed above, the reagent blank must contain less than the Contract Required Detection Limit of any single HSL analyte. If a laboratory reagent blank exceeds criteria, the contractor must consider the analytical system out of control. The source of the contamination investigated and appropriate corrective measures must be taken and documented.

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. Samples analyzed where surrogate recovery(ies) in the blank are outside of contract required windows will require reanalysis of all affected samples at no additional cost to the Agency.

4.4.2 Sample Surrogate Spike Recovery

When the surrogate recovery of any one surrogate compound is outside of the contract required surrogate recovery limits (listed in Table 4.2) for a sample, it is the responsibility of the Contractor Laboratory to establish that the deviation is not due to contractor laboratory problems. The quality control windows are calculated using program generated analytical data. It is expected that 5-15 percent of the surrogate recovery data may fall outside of these windows, and will require recalculation and/or reextraction/reanalysis on the part of the Laboratory.

4.4.2.1 The contractor laboratory shall document, (in this instance, document means to write down and discuss problem and corrective action(s) taken in the Case Narrative, see Exhibit B for more details) deviations outside acceptable quality control limits by taking the following actions:

4.4.2.1.1 Check calculations to assure there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc.; and, check instrument performance.

4.4.2.1.2 Recalculate or reanalyze the sample or extract if the steps in 4.4.2.1.1 fail to reveal a problem. If reanalysis of the sample or extract solves the problem then only submit the sample data from the analysis with surrogate spike recoveries within the contract windows.

4.4.2.1.3 Reextract and reanalyze the sample if none of the above are a problem.

4.4.2.1.3.1 Report the surrogate spike recovery data and the sample data from both extractions according to paragraph 4.5.

4.5 Documentation

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

* Reagent Blank Analysis
* Matrix Spike Analysis
* Matrix Spike/Duplicate Analysis
* All sample reanalyses that substantiate a matrix effect

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

4.4 Treatment of surrogate spike recovery information is according to paragraphs 4.4.1 through 4.4.2.

4.4.1 Reagent Blank Surrogate Spike Recovery

When the surrogate recovery of any one surrogate compound is outside of the contract required surrogate recovery limits (listed in Table 4.2) for a reagent blank, the laboratory must take the following actions:

TABLE 4.2. CONTRACT REQUIRED SURROGATE SPIKE RECOVERY LIMITS

Fraction	Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
VOA	Toluene-d_8	86-119	50-160
VOA	4-Bromofluorobenzene	85-121	50-160
VOA	1,2-Dichloroethene-d_4	77-120	50-160
BNA	Nitrobenzene-d_5	41-120	20-140
BNA	2-Fluorobiphenyl	44-119	20-140
BNA	p-Terphenyl-d_{14}	33-128	20-150
BNA	Phenol-d_5	15-103	20-140
BNA	2-Fluorophenol	23-121	20-140
BNA	2,4,6-Tribromophenol	10-130	10-140
Pest.	Dibutylchlorendate	(48-136)*	(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.

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

4.4.1.2 Recalculate or reinject/repurge the blank or extract if steps in 4.4.1.1 fail to reveal the cause of the non-compliant surrogate recoveries.

4.4.1.3 Re-extract and reanalyze the blank.

4.4.1.4 If the measures listed in 4.4.1.1 thru 4.4.1.3 fail to correct the problem, the analytical system must be considered out of control. The problem MUST be corrected before continuing.

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.

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

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 non-spiked HSL 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. The results for non-spiked HSL 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. (See Exhibit B, Deliverables, Section III, for complete instructions on the completion of Form III.)

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

Part 5 Matrix Spike/Matrix Spike Duplicate Analysis (MS/MSD)

5.0 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 analysis. 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/matrix spike duplicate must be performed once each Case, with every twenty (20) samples of similar concentration and/or similar sample matrix, whichever is greater.

5.2 Use the compounds listed in Table 5.1 to prepare matrix spiking solutions according to protocols described in Exhibit D. The analytical protocols in Exhibit D require that a uniform amount of matrix spiking solution 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 sample.

TABLE 5.1. MATRIX SPIKING SOLUTIONS

Base/Neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Di-n-butyl Phthalate	4-Chloro-3-Methylphenol
Pyrene	4-Nitrophenol
N-Nitroso-Di-n-Propylamine	
1,4-Dichlorobenzene	

Pesticides		Volatiles	
Heptachlor	Lindane	Chlorobenzene	1,1-Dichloroethene
Aldrin	Endrin	Toluene	Trichloroethene
Dieldrin	4,4'-DDT	Benzene	

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.

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 QC was completed, it is necessary to conduct an instrument tune and calibration check analysis (described in Part 2 of this Exhibit). 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. 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.

Retention time and EICP area records shall be maintained in the form of control charts by the laboratory as part of its internal quality control and made available for inspection by on-site EPA personnel.

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 semi-volatile HSL compounds). If any compound in any sample exceeds the analytical range, that sample must be diluted, the internal standard concentration readjusted, and the sample reinjected, as described in specific methodologies in Exhibit D.

6.1.3 Qualitative Analysis - The target compounds listed in the Hazardous Substances List (HSL), 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 $\pm$0.06 RRT units of the

TABLE 5.2. MATRIX SPIKE RECOVERY LIMITS*

Fraction	Matrix Spike Compound	Water*	Soil/Sediment*
VOA	1,1-Dichloroethene	61-145	59-172
VOA	Trichloroethene	71-120	62-137
VOA	Chlorobenzene	75-130	60-133
VOA	Toluene	76-125	59-139
VOA	Benzene	76-127	66-142
BN	1,2,4-Trichlorobenzene	39-98	38-107
BN	Acenephthene	46-118	31-137
BN	2,4-Dinitrotoluene	24-96	28-89
BN	Di-n-butyl Phthalate	11-117	29-135
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
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 6 Sample Analysis

6.0 SUMMARY

This section does not replace or supercede specific analytical methods or QA/QC activities described in previous sections. The intent of this subsection is to provide the Contractor laboratories with a brief summary of on-going QC activities involved with sample analysis. Specific references are provided to help the Contractor laboratories meet specific Reporting and Deliverables required by this IFB.

6.1.5 Reporting and Deliverables - Refer to Exhibit B of this document for specific details on contract deliverables and raporting formats. Exhibit B contains specific instructions for completing all required Forms, as well as a detailed itemization of reporting and deliverables requirements.

Part 7 Pesticide QA/QC Requirements

7.0 SUMMARY

This section describes the additional Quality Control procedures required during the analysis of pesticide/PCBs that are not covered in Parts 3, 4, and 5 of this Exhibit.

7.1 The Laboratory must perform the following:

7.1.1 Reagent Blank analysis as per Exhibit E, Section III, Part 3.

7.1.2 Matrix Spike/Matrix Spike duplicate analysis as per Exhibit E, Section III, Part 5.

7.1.3 Spike all standards, samples, blanks, matrix spike and matrix spike duplicate samples with the surrogate spike compound (dibutylchlorendate) as per Exhibit E, Section III, Part 4.

7.2 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 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.

7.2.1 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. Conditions listed in Table 7, Exhibit D, Section IV may be used to achieve this criteria.

7.2.2 Establish retention time windows as follows:

7.2.2.1 Make three injections of all single component pesticide mixtures, multi-response pesticides and PCBs throughout the course of a 24-hour period.

7.2.2.2 Verify the retention time shift for dibutylchlorendate in each standard. The retention time shift between the initial and subsequent standards must be less than a 2 percent difference for packed columns (<0.3 percent for capillary column). If this criterion is not met, continue injecting replicate standards to meet criteria.

7.2.2.3 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.

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 or DFTPP tuning requirements listed in Exhibit E, Section III, Part I must be met on the Contractor's 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, Section IV).

6.1.3.3 A library search shall be executed for non-HSL sample components for the purpose of tentative identification. For this purpose, the most recent available version of the EPA/NIH Mass Spectral Library should be used.

6.1.4 Quantitation

6.1.4.1 HSL components identified shall be quantitated by the internal standard method. The internal standard used shall be the ones assigned in Tables 2.1 and 2.2, Exhibit E. The EICP area of characteristic ions of HSL analytes are used (Exhibit D, Section IV).

6.1.4.2 An estimated concentration for non-HSL 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 Surrogate Recoveries (Exhibit E, Section III, Part 4) - Calculate surrogate standard recovery 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). If recovery is outside contractual limits, take specific steps listed in Exhibit E, Surrogate Spike Recoveries.

6.1.4.4 Matrix Spike/Matrix Spike Duplicate - Calculate matrix spike and matrix spike duplicate percent recovery for all compounds. Report results on properly using Form III. Calculate Relative Percent Differences (RPD's) for all matrix spiking compounds and report results on Form III. Ensure that the proper frequency of MS/MSD analysis is maintained.

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).

7.3.1.2 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.

7.3.1.2.1 Calculate the percent breakdown for Endrin and/or 4,4'-DDT on the mixed phase (1.5% OV-17/1.95% OV-210 or equivalent) GC column using Equations 7.3 and 7.4. The percent breakdown for Endrin or 4,4'-DDT must not exceed 20 percent. Corrrective action must be taken before analysis continues.

$$\% \text{ breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100 \qquad \text{Eq. 7.3}$$

$$\% \text{ breakdown for Endrin} = \qquad \text{Eq. 7.4}$$

$$\frac{\text{Total Endrin degradation peak areas (Endrin Aldehyde + Endrin Ketone)}}{\text{Total Endrin Peak Area (Endrin + Endrin Aldehyde + Endrin Ketone)}} \times 100$$

7.3.1.2.2 Calculate the percent breakdown for Endrin and/or 4,4'-DDT on the OV-1 or equivalent GC column using Equations 7.3 and 7.4 The percent breakdown for Endrin or 4,4'-DDT must not exceed 20 percent. Corrective action must be taken before analysis continues.

7.3.1.2.2.1 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 7.5. The combined Endrin/4,4'-DDT percent breakdown must not exceed 20 percent. Corrective action must be taken before analysis continues.

NOTE: The term peak height may be substituted for the term peak area.

7.2.2.3.1 Plus or minus three times the standard deviation of the absolute retention times for each pesticide/PCB will be used to define the retention time window; however, 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.

7.2.2.3.2 In those cases where the standard deviation for a particular pesticide/PCB is zero, the laboratory may substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

7.2.2.4 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.

7.3 Primary GC Column Analysis

7.3.1 Evaluation Standard Mixtures

7.3.1.1 Prepare Evaluation Standards A, B, and C (Aldrin, Endrin, 4,4'-DDT and Dibutylchlorendate) at the 3 concentration levels described in Exhibit D. Analyze the three Evaluation Standards sequentially at the beginning of each twenty-four (24) hour period (See Table 7.1).

7.3.1.1.1 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 7.1.

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak}}{\text{Mass Injected (in nanograms)}} \qquad \text{Eq. 7.1}$$

7.3.1.1.2 Using the Calibration Factors from 7.3.1.1.1. above, calculate the percent relative standard deviation (%RSD) for each compound at the three concentration levels using Equation 7.2. The percent relative standard deviation for Aldrin, Endrin, and Dibutylchlorendate must be $\leq$ 10 percent. If the %RSD exceeds 10% for 4,4'-DDT, see Section 7.5.4.4.

$$\% \text{ Relative Standard Deviation} = \frac{SD}{\bar{x}} \times 100 \qquad \text{Eq. 7.2}$$

NOTE: The term peak height may be substituted for the term peak area.

7.3.2 Individual Standard Mixture A or B

7.3.2.1 Prepare Individual Standard Mixtures A or B containing all single-component pesticides. These may be in one mixture or divided into the groups suggested in Exhibit D, which are recommended to prevent overlap of compounds on the two packed columns. Prepare separate solutions of all multiresponse pesticides and PCBs. (Arochlor 1016 and Arochlor 1260 may be combined in a single mixture.)

7.3.2.2 Analyze Individual Standard Mixture A or B and all multi-response pesticide/PCB's at the beginning of each 24 hour period (see Figure 7.1) and analyze Individual Standard Mixture A or B after 12 hours have elapsed or whenever sample analysis is completed, whichever comes first. The Calibration Factor for each standard, (Individual Standard Mix A or B) (Equation 7.6), must not exceed a 15 percent difference for a quantitation run nor exceed a 20 percent difference for a confirmation run during the 12 hour period. Calculate percent difference using Equation 7.7. Deviations greater than 15 percent require the laboratory to repeat the samples analyzed following the quantitation standard that exceeded the criteria.

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak*}}{\text{Mass injected (in nanograms)}} \qquad \text{Eq. 7.6}$$

* For multiresponse pesticides/PCBs use the total area of all peaks used for quantitation.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100 \qquad \text{Eq. 7.7}$$

where R_1 = Calibration Factor from first analysis

R_2 = Calibration Factor from second analysis

7.4 Sample Analysis (Primary GC Column)

7.4.1 Samples are analyzed per the sequence described in Figure 7.1.

Note: The term peak height may be substituted for the term peak area.

Combined % breakdown = Eq. 7.5

$$\frac{\text{Total Endrin/DDT degradation peak areas (DDD, DDE, Endrin Aldehyde + Endrin Ketone)}}{\text{Total Endrin/DDT peak area (Endrin, Endrin Aldehyde, Endrin Ketone, DDT, DDD, DDE)}}$$

7.3.1.3 Suggested Maintenance

Corrective measures may require any one or more of the following remedial actions:

• 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 wash 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.

• Capillary columns - Clean and deactivate the glass injection port insert or replace with a cleaned and 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.

• Metal Injector Body - Turn off the oven and remove the analytical column when 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 noticable 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.

NOTE: The term peak height may be substituted for the term peak area.

7.4.1.2 Evaluate the GC column throughout the analysis of samples by injecting Evaluation Standard Mix B at the frequency outlined in Figure 7.1.

7.4.1.2.1 Calculate the percent breakdown for 4,4'-DDT and Endrin according to 7.3.1.2. Take corrective action when the breakdown for 4,4'-DDT or Endrin exceeds 20 percent.

7.5 Confirmation Analysis (GC/EC)

7.5.1 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 24-hour sequence described in Figure 7.1 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 in Section 7.5.4.

7.5.2 Separation should be $\geq$ 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 criteria cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

7.5.2.1 For a fused silica capillary (FSCC) confirmation, there must be $\geq$ 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

7.5.3 All QC specified previously must be adhered to, i.e., the $\geq$ 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.

7.5.4 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 confirmed and quantitated. There are four combinations of pesticides that could occur, therefore, the following sequences must be followed depending on the situation.

7.5.4.1. 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 $\leq$ 10 % RSD, use the appropriate equation in Exhibit D for calculation. If > 10 % RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

FIGURE 7.1. 24 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. Tech. chlordane
8. Aroclors 1016/1260
9. Aroclor 1221
10. Aroclor 1232
11. Aroclor 1242
12. Aroclor 1248
13. Aroclor 1254
14. 5 samples
15. Evaluation Standard mix B
16. 5 samples
17. Individual Standard Mix A or B
18. 5 samples
19. Repeat the above sequence starting with Evaluation Standard Mix B (step 15 above).
20. Pesticide/PCB analysis sequence must end with Individual Standard Mix A or B regardless of number of samples analyzed.

* These may be one mixture.

7.4.1.1 The retention time shift for Dibutylchlorendate must be evaluated after the analysis of each sample. The retention time shift may not exceed a 2 percent difference for packed GC columns between the initial standard analysis and any sample analyzed during the 12 hour period. The percent difference for capillary columns must not exceed 0.3 percent (Equation 7.8).

$$\text{Percent Difference (\%D)} = \frac{RT_I - RT_S}{RT_I} \times 100 \qquad \text{Eq. 7.8}$$

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.

7.5.7 Inject the reagent blank (extracted with each set of samples) on every GC and GC column that the samples are analyzed on.

7.6 GC/MS Pesticide/PCB Confirmation

7.6.1 Any pesticide/PCB confirmed by two dissimilar GC columns must also be confirmed by GC/MS provided the concentration in the final sample extract is sufficient for GC/MS analysis (based on laboratory GC/MS detection limits).

7.6.1.1 Pesticides/PCBs may be confirmed utilizing the extract prepared for semi-volatile GC/MS analysis; however, the absence of pesticide/PCBs in the semi-volatile extract would require the analysis of the pesticide (fraction) extract.

7.6.2 The tuning and mass calibration criteria for DFTPP (50 ng) MUST be met prior to any confirmation of Pesticide/PCBs is undertaken.

7.6.3 The pesticide/PCB sample extract(s), the associated pesticide/PCB blank(s), and reference standard(s) must be analyzed by GC/MS.

7.7 Documentation

7.7.1 See Exhibit B for complete instructions for the completion of all required forms and the Deliverable Index for all reporting and deliverables requirements.

7.5.4.2 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 7.5.4.1 for each compound to be quantitated.

7.5.4.3 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 7.5.4.1 for each compound to be quantitated.

7.5.4.4 Other pesticides/PCBs plus DDT series and/or toxaphene - Being 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% RSD and/or degradation exceeds the criteria, corrective maintenance as outlined in paragraph 7.3.1.3 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 7.5.4.2 (do not repeat Evaluation Mix B). If none of the DDT series is to be quantitated and DDT exceeds the 10% RSD, simply record the % RSD on the proper form. Anytime toxaphene is to be quantitated, follow 7.5.4.1.

7.5.5 After the linearity standards required in 7.5.4 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 7.5.6 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 following the standard that exceeds the criteria.

7.5.6 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 each 10 samples). The alternating standard's ratio of the response to the amount injected must be within 15 percent of each other if quantitation is performed. Deviations larger than 15 percent require the laboratory to repeat the samples analyzed following the standard that exceeds the criteria. The 15 percent criteria only pertains to compounds being quantitated.

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.

Samples must also be repeated if the degradation of either DDT and/or Endrin exceed 20 percent 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.

QUALITY ASSURANCE MATERIALS BANK
REQUEST FOR REFERENCE STANDARDS

MAIL TO: U.S Environmental Protection Agency
Quality Assurance Materials Bank (MD-8)
Research Triangle Park, NC 27711 USA

Date _____

Telephone:
Requests ONLY: (919) 541-4019
(FTS) 629-4019
Information: (702) 545-2690
(FTS) 545-2690
Technical Assistance: (919) 541-3951
(FTS) 629-3951

Date Request Received _____
Date of Shipment _____
Laboratory Code Number _____
Request Number _____
Verified _____
THIS BLOCK FOR AGENCY USE ONLY

The following reference standards are required for our program:

Number Required	Standard Code Number	Compound(s)	Solvent	Purity	Concentration (µg/ml)

Please complete this form in full, PRINTING OR TYPING name and address. Use black ink if possible. Use back of sheet to complete all if necessary. No other letter is needed.

Name and Address of laboratory: _____

_____

_____

_____

_____
Requester's Name

IMPORTANT:

I certify that the calibrated sample(s) requested are to be used only in this laboratory by qualified personnel for the purpose of developing or checking analytical procedures and/or for the calibration of instrumentation.

_____
Date

_____
Signature

Request for Reference Standards

SECTION IV - ANALYTICAL STANDARDS

The Environmental Protection Agency's Quality Assurance Materials Bank will supply primary standards (calibration standards, surrogate standards, matrix spiking standards, and internal standards), contingent upon their availability, for traceability and quantitative verification of Contractor standards. It is emphasized that these primary standards are for traceability only. There are insufficient qnantities to have these available to serve as working standards. The contract laboratory is responsible for preparing its own working standards from commercial sources.

Caution should be exercised in the mixing of theee standards together, particularly the multicomponent standards. Chemical reactions such as ecid/base reactions, Schiff base formations (reacrions of aldehydes and ketones with primery amines), hydrolysis, isotopic exchange, and others may occur.

EPA contract laboratories can call or write directly to the QAMB (address and phone number on the following request form) to obtain reference standerds. Standards will be provided based on the reasonableness of the request and rheir availability. Any request from a commercial laboratory that is not currently under contract to EPA will be denied.

Upon award uf a contract, a list of available standards will be provided by the EMSL-LV upon request.

Laboratory _____ Date _____

Quarter ple (circle one): 1 2 3 4 FY_____

I. Substance List (HSL) Results — Points Awarded

A. Identifications (maximum of 40 points possible)
(number of compounds not identified (____) x 40/
number of compounds in study = _____ deducted) _____

B. (maximum of 40 points possible)
(number of compounds not within acceptance
(____) x 40/number of compounds in
study = _____ deducted) _____

C. HSL false positive identifications above
contract-specified objective limit (maximum
of 15 points possible) (number of false
positives (____) x 15/number of compounds
in study = _____ deducted) _____

II. Non-HSL Results

A. Identifications (max of 30 points possible) _____
(number of non-HSL not identified (____) x 30/
number of compounds in study _____ deducted)

B. Non-HSL false positive identifications (maximum _____
of 15 points possible) (number of false positives
(_____) x 15/number of compounds in study =
_____ deducted)

Maximum Score for Sections I & II = _____
Raw Score for Sections I & II = _____
Raw Percent for Sections I & II = _____

Final Score _____

III. Timeliness criteria (minus 1% from Raw Score for each day data package is delivered late). Late is defined as 31 days or more after the day of sample receipt = _____ deducted.

NOTE: This Figure is a sample only. The actual form (scoring system) used may vary depending on sample or study design or as a result of modifications to the contract.

Figure 1. Performance evaluation sample data [illegible]

SECTION V - LABORATORY EVALUATION PROCEDURES

This document outlines the procedures which will be used by the Project Officer or his authorized representative to conduct laboratory audits to determine the laboratory's ability to meet the terms and conditions of this contract. The evaluation process incorporates two major steps: 1) evaluation of laboratory performance, and 2) onsite inspection of the laboratory to verify continuity of personnel, instrumentation and quality control requirements contained in the IFB. The following is a description of these two steps.

Part 1 Evaluation of Laboratory Performance

1.0 Performance Evaluation Sample Analysis

1.1 The Performance Evaluation (PE) sample set will be sent to a participating laboratory on a quarterly basis to verify the laboratory's continuing ability to produce acceptable analytical results. These samples will be provided either single blind (recognizable as a PE material and of unknown composition), or double blind (not recognizable as a PE material and of unknown composition). Contractors are required to return PE analytical data within thirty (30) calendar days of receipt.

1.2 When the PE data are received, results will be scored routinely for identification and quantitation, according to the elements and weighting factors shown in Figure 1. Results of these scorings will be provided for the contractor via coded evaluation spread sheets by compound classes. The government may adjust the scores on any given PE sample to compensate for unanticipated difficulties with a particular sample. If a laboratory is remiss in its ability to perform acceptably on the PE sample, the government may conduct an on-site visit and a full data audit, so that corrective action may be taken immediately.

Timeliness in delivering PE sample data to the government is essential and is reflected in the deduction of points from the gross score (Figure 1) for late data submissions. Late is defined as 31 days or more from the documented day of sample receipt.

2.0 Organic Data Audit

2.1 Organic data audits are conducted on CLP Contractor's Reporting and Deliverables packages EMSL-LV. The organic data audit provides the Agency with an in-depth inspection and evaluation of the Case data packages with regard to achieving contractual compliance and QA/QC acceptability.

2.2 The Agency may use statistical evaluations such as the Military Standard (Mil Std) 105D as the audit mechanism. Mil Std 105D can be used to evaluate the quality of CLP data by classifying errors into three categories depending on the gravity of the defect. A critical defect affects the

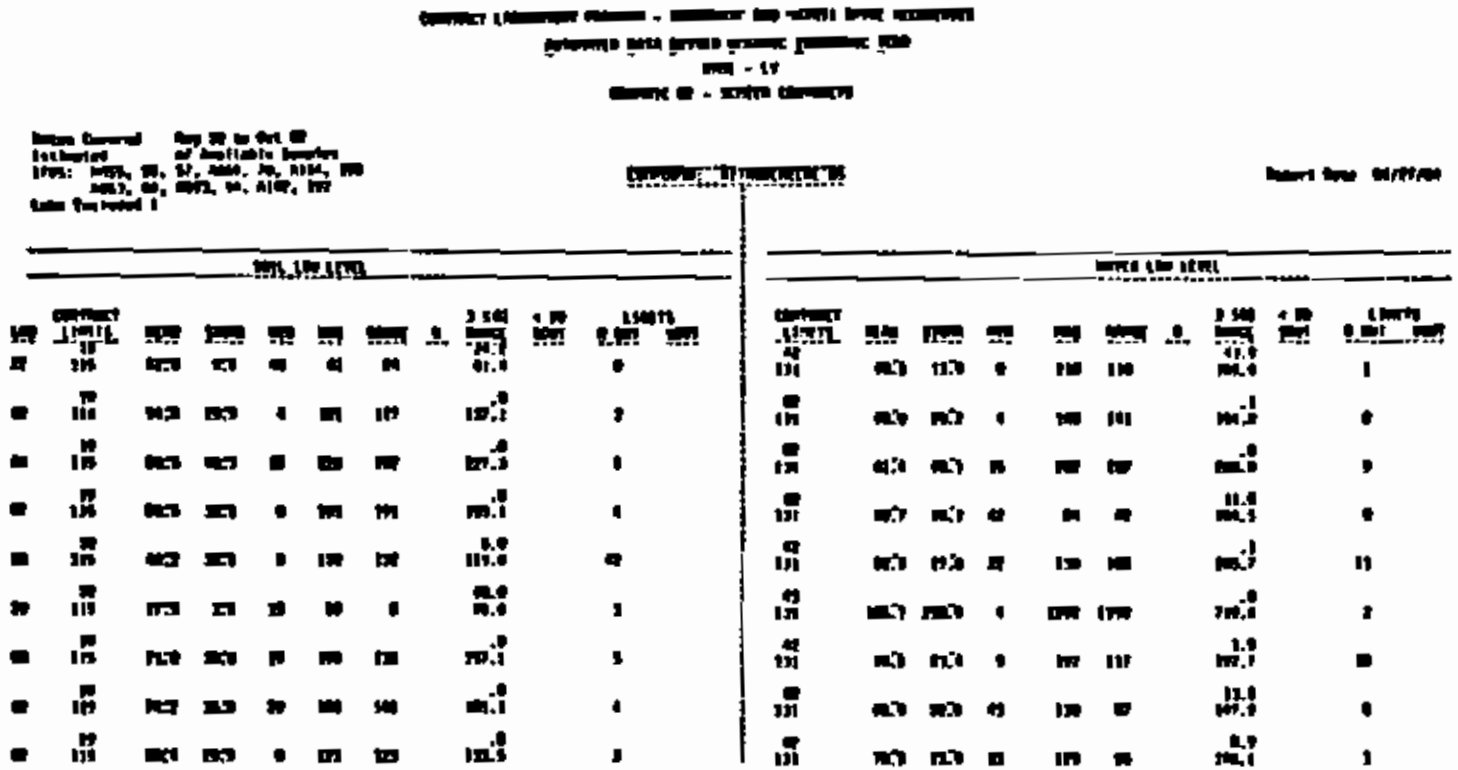

Figure 2. Surrogate and matrix spike recoveries.

validity of an entire Case; a major defect affects the validity of a single sample or group of samples within a specific Case; a minor defect can affect the technical quality of the data, but should be easily resolved.

Mil Std 105D may be used to determine a specific acceptable quality level (AQL) based on submitted data from all contract laboratories. The Agency can then identify individual laboratories consistently below the AQL, identify specific problems, and address the problems in a timely fashion through an increase in the data audit procedure or through additional on-site evaluations or a combination of both. It is recommended that all identified defects be corrected or replaced with acceptable material.

3.0 Trend Analysis

Monitoring of quality control data produced during contract laboratory analysis is performed by entry into a computer data base, Automated Data Review Organic, Inorganic, TCDD (ADROIT). Data entry is accomplished from the contract specified forms. Deviation from the contractually specified forms is unacceptable in content or order. Production of these data base reports has been continuous since November 1982 and has been the basis of protocol revisions. The reports now provide the capability of trend analysis in the quality control data produced from Contract laboratories. These reports are capable of producing laboratory, case, and sample number specific data anomalies or trends for the following areas:

Organic	
Surrogate Spikes	* Tuning
Matrix Spike	* Calibration
Blanks	
Duplicates	

* Under development

3.2 Program-wide statistical results are used to rank laboratories in order to observe the relative performance of each laboratory in a given protocol against its peers. These reports are also used to evaluate trends within laboratories. The results of these trend analyses are included in overall evaluation of laboratory performance.

3.3 Laboratory performances over time will be monitored using these trend analysis techniques to detect departures of laboratory output from required or desired levels of quality control performance level.

3.4 Examples of some of these reports are shown in Figures 2 thru 5 for information purposes only. The government reserves the right to modify the content and/or format of these reports.

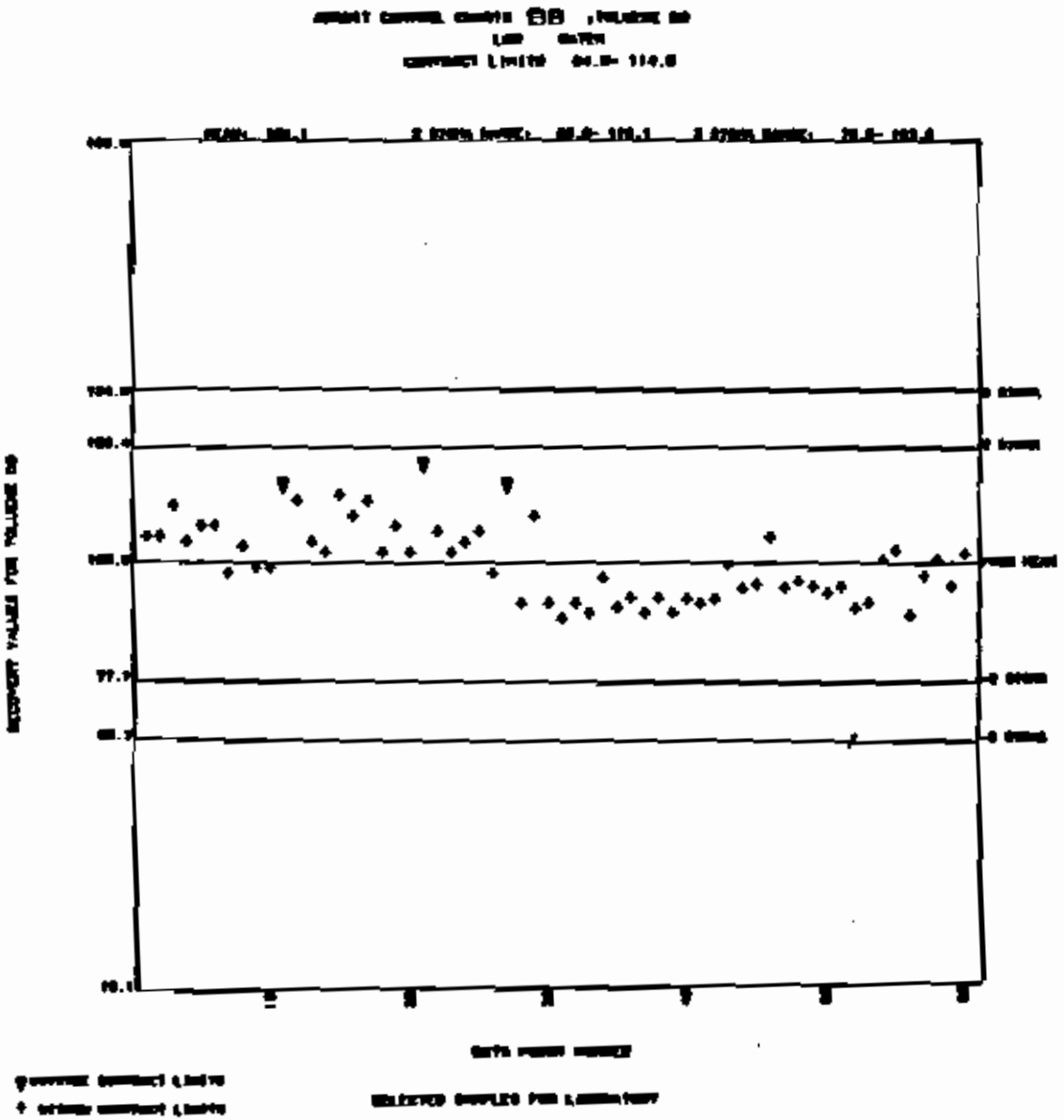

Figure 4. Adroit control charts BB.

CONTRACT LABORATORY PROGRAM
AUTOMATED DATA REVIEW ORGANIC, INORGANIC, TCDD
ORGANIC TUNING AND CALIBRATION SUMMARY

EXCEPTIONS

Lab 88 Case 2304 Contract Number 68-0000

Instr. 2 BFB 2/6/84-0830			Instr. 3 DFTPP 2/6/84-1800		
m/e	Criteria	Reported	m/e	Criteria	Reported
50	15.0-40.0% of base peak(95)	48.0	365	>1.00% of mass 198	0.42

SAMPLES AFFECTED			SAMPLES AFFECTED		
C2401	2/6/84	0948	C2401	2/6/84	1852
C2402	2/6/84	1055	C2407	2/6/84	1948
C2403	2/6/84	1215	C2403	2/6/84	2057
C2404	2/6/84	1320	C2404	2/6/84	2200

SAMPLES WITH NO TUNE SUBMITTED
WITHIN 12 HOURS

BFB			DFTPP		
C2412	2/6/84	2130	C2422	2/7/84	0010

Instrument I.D. for tune does not match Instrument I.D. for analysis.

Sample	Instrument I.D. BFB	Instrument I.D. VOA Analysis
C2424	2	4

Form 8

Figure 3. Organic tuning summary.

Part 2. On-site Laboratory Evaluation

The on-site laboratory evaluations help to assure that all the necessary quality control is being applied by the laboratory in order to deliver a quality product. Quality assurance evaluations allow the evaluators to determine that:

1) The Organization and Personnel are qualified to perform assigned tasks,

2) Adequate Facilities and Equipment are available,

3) Complete Documentation, including chain-of-custody of samples is being implemented,

4) Proper Analytical Methodology is being used,

5) Adequate analytical Quality Control, including reference samples, control charts, and documented corrective action measures, is being provided, and

6) Acceptable Data Handling and documentation techniques are being used.

The on-site visit also serves as a mechanism for discussing weaknesses identified through the Performance Evaluation sample analysis. Lastly, the on-site visit allows the evaluation team to determine if the laboratory has implemented the recommended and/or required corrective actions, with respect to quality assurance, made during the previous on-site visit.

The following describes the protocol which is followed during a laboratory evaluation. Included is an Organic Laboratory Evaluation Checksheet (OLEC). A similar OLEC will be used in future on-site laboratory evaluations in order to maintain a continuous record. The government reserves the right to change the OLEC as changing conditions dictate.

2.1. Event Sequence for the Laboratory Evaluation

I. Meeting with Laboratory Manager and Project Manager

A. Introduction

B. Discuss purpose of visit

C. Review of personnel changes

II. Review of Previous Trip Report

The most recent report is reviewed to verify that all previously identified problems have been corrected.

Organic Control Chart Raw Data

* Outside Contract Limits 84.00- 114.00

Automated Data Review Organic, Inorganic, TCDD

EMSL-LV

For 88 Toluene 08 Low Water 01-Feb-84

POINT	CASE	SAMPLE NO.	QC NO.	CONTRACT	VALUE	
1	1954	F2428MS	-1	68-01-6724	106.000	
2	1954	F2389	-1	68-01-6724	106.000	
3	1954	F2388	-1	68-01-6724	112.000	
4	1954	MB1	-1	68-01-6724	105.000	
5	1954	F2428	-1	68-01-6724	106.000	
6	1954	F2428MSD	-1	68-01-6724	108.000	
7	2009	MB03	-1	68-01-6724	99.000	
8	2033	A1761	-1	68-01-6724	104.000	
9	2033	A1762	-1	68-01-6724	100.000	
10	2033	A1763MSD	-1	68-01-6724	100.000	
11	2033	A1760	-1	68-01-4724	116.000	*
12	2033	MB18	-1	68-01-6724	113.000	
13	2033	A1763	-1	68-01-6724	105.000	
14	2033	A1763MS	-1	68-01-6724	103.000	
15	2033	MB17	-1	68-01-6724	114.000	
16	2087	B2425	-1	68-01-6724	110.000	
17	2087	B2431	-1	68-01-6724	113.000	
18	2087	B2432	-1	68-01-6724	103.000	
19	2087	B2423	-1	68-01-6724	100.000	
20	2087	MB23	-1	68-01-6724	103.000	
21	2087	B2429	-1	68-01-6724	120.000	*
22	2087	B2429	-1	68-01-6724	107.000	
23	2087	MB26	-1	68-01-6724	103.000	
24	2087	B2426	-1	68-01-6724	105.000	
25	2087	B2427	-1	68-01-6724	107.000	
26	2087	B2427MS	-1	68-01-6724	99.000	
27	2087	B243C	-1	68-01-6724	116.000	*
28	2087	B2427MSD	-1	68-01-6724	93.000	
29	2087	B2424	-1	68-01-6724	110.000	
30	2101	F2423	-1	68-01-6724	93.000	
31	2101	F2384	-1	68-01-6724	90.000	
32	2101	F2434MSD	-1	68-01-6724	93.000	
33	2101	F2434MS	-1	68-01-6724	91.000	
34	2101	F2382	-1	68-01-6724	98.000	
35	2101	F2439	-1	68-01-6724	82.000	
36	2101	F2434	-1	68-01-6724	94.000	
37	2101	F2383	-1	68-01-6724	91.000	
38	2101	MB2	-1	68-01-6724	94.000	
39	2101	F2437	-1	68-01-6724	91.000	
40	2224	C3484MSD	-1	68-01-6724	93.900	
41	2224	C3484	-1	68-01-6724	92.900	
42	2224	C3484MS	-1	68-01-6724	93.800	
43	2224	C3403	-1	68-01-6724	100.700	
44	2224	C3401	-1	68-01-6724	96.000	
45	2224	C3402	-1	68-01-6724	96.900	
46	2224	C3400	-1	68-01-6724	106.000	
47	2224	C3494	-1	68-01-6724	86.100	

Figure 5. Organic control chart raw data.

Organic

Laboratory Evaluation Checksheet

III. Laboratory Tour

At this stage of the evaluation process, a laboratory tour is performed. The tour follows the path of a sample starting from sample receipt to final compilation, review and distribution of rhe data genereted by sample analysis. Photographs may be taken during the tour.

IV. Post Laboratory Team Caucus

The evaluation team caucuses separately in order to collate their observations as a result of the leboratory tour. Both positive and negative items are diecuseed.

V. Review of Data Audit Report(s)

Questions or problems noted in the data audit report, performance evaluation etudies, or comments from users of the data are discussed at this stage of the evaluation process. The review of data generated by the laboratory may neceseitate complete examination of all documentation associated with the sample(s) in queetion.

VI. Documentation Procedures

An avidentiary audit of chain-of-custody end aimilar procedures is conducted by the Contract Evidence Audit Team (CEAT), which is under contract to the USEPA National Enforcement Investigation Center, Denver, Colorado.

VII. Predebriefiog Caucus

The avaluation ream caucus and determines the problems and/or positive items ro be relseaed to the contractor. Problem areas and iteme to be included in the evaluation raport or for considerarion by the Project Officer are discussed.

VIII. Debriefing

A technical summary of observatione, and the comments of the NEIC representativas, are presanted to the Contractor. The Contractor is then eolicited for responaes. A eummarization of itams to be corrected within an agreed timaframe is reviewed.

Attachment I

Laboratory Evaluation Check List

ORGANIZATION AND PERSONNEL (page 1 of 2)

	YES	NO	COMMENT
Laboratory Director or Project Manager (individual responsible for overall technical effort): Name: _____			
GC/MS Operator: Name: _____ Experience: 9 months minimum requirement			
GC/MS Spectral Interpretation Expert: Name: _____ Experience: 2 years minimum requirement			
Purge and Trap Expert: Name: _____ Experience: 6 months minimum requirement			
Extraction Concentration Expert: Name: _____ Experience: 1 year minimum requirement			
Pesticide Residue Analysis Expert: Name: _____ Experience: 2 years minimum requirement			

FACSIMILE

Laboratory: _____

Date: _____

T[illegible]on: _____

[illegible]umbe[illegible] _____

Contract Title: _____

Perf[illegible] _____

Name	Title

Laboratory Evaluation Team:

Name	

II. Sample Receipt and Storage Area

ITEM	YES	NO	COMMENT
Is a sample custodian designated? If yes, name the sample custodian. Name _____			
Are written Standard Operating Procedures (SOP) developed for receipt and storage of samples?			
Is the appropriate section of the SOP available to the analyst in the sample receipt/storage area?			
Are the sample shipping containers opened in a manner which prevents possible laboratory contamination?			
Are samples that require refrigeration stored in such a way as to maintain preservation?			
Are volatile samples stored separately from semi-volatile samples?			
Are adequate facilities provided for storage of samples, including cold storage?			
Is the temperature of the cold storage recorded daily in a logbook?			

I ORGANIZATION AND PERSONNEL (Page 2 of 2)

ITEM	YES	NO	COMMENT
Do personnel assigned to this project have the appropriate level and type of experience to successfully accomplish the objectives of this Project?			
Is the organization adequately staffed to meet project commitments in a timely manner?			
Was the Quality Assurance Officer available during the evaluation? Name: _____			
Does the laboratory Quality Assurance Officer report to senior management officials?			
Was the Project Manager available during the evaluation?			

Additional Comments

III. Sample Preparation Area

When ...uring the facilities, give special attention to: (a) the over... ...nce of organization and neatness, (b) the proper maintenance of f... a... ...nstrumentation, (c) the general adequacy of the facilities to ... th... ...quired work.

ITEM	YES	NO	COMMENT
Is the l... ...rato... ...intained in a clean and organized ...			
Does the ... ...to... ... have adequate workspace ... ..., ...ar feet of unencumbered b... ...pace per ...lyst)?			
Are the toxic ch... ...handling areas either a stainless steel b... ... an im... ...material covered with absorbent materi...			
Are contamination-free ... ...s p... ...ded ... trace level analytical work?			
Are contamination-free work areas ... ... for the handling of toxic materials ... ...ove h...			
Are exhaust hoods provided to allow ... contamination-free work with volati... ...teri...			
Is the air flow of the hoods periodical... checked and recorded?			
Are chemical waste disposal policies/proced... adequate?			
Does the laboratory have a source of distilled/ demineralised water?			
Is the conductivity of distilled/demineralized water routinely checked and recorded?			

II. Sample Receipt and Storage Area (Continued)

ITEM	YES	NO	COMMENT
[illegible] sample receipt/storage and temperature [illegible] maintained in a manner consistent with CLP?			
Has [illegible] supervisor the individual maintaining the notebook periodically examined and reviewed the notebook [illegible]dically, and signed his/her name thereto [illegible]gether with the date and appropriate [illegible]hen [illegible]hether or not the notebook [illegible]n an appropriate manner.			

Additional Comments:

III. Sample Preparation Area (Continued)

ITEM	YES	NO	COMMENT
th[illegible]alys[illegible] record bench data in a neat and accura[illegible]anner?			
Are [illegible] separately from sample ex[illegible]			
Is the SOP [illegible]esaware washing posted at the cleaning st[illegible]			
Is the tempera[illegible]t the re[illegible]erations/freezer recorded daily[illegible]			

Additional Comments

III. Sample Preparation Area (Continued)

ITEM	YES	NO	COMMENT
Does the laboratory supervisor document that trace-free water is available for preparation of standards and blanks?			
Is the analytical balance located away from draft and areas subject to rapid temperature changes?			
Has the balance been calibrated within one year by a certified technician?			
Is the balance routinely checked with class S weights before use and the results recorded in a logbook?			
Are the solvent storage containers properly vented in order to prevent possible laboratory contamination?			
Is the appropriate portion of the SOP available to the analyst at the sample preparation area?			
Are reagent grade or higher purity chemicals used to prepare standards?			
Are fresh analytical standards prepared with a frequency consistent with good QA?			
Are reference materials properly labeled with concentrations, date of preparation, and the identity of the person preparing the sample?			
Is a standards preparation and tracking logbook maintained?			

A. GC/MS/DS Instrumentation

ITEM	YES	NO	COMMENT
Are manufacturer's operating manuals readily available to the operator?			
Is [illegible] protocol in use by the operator?			
Are calibration results kept in a permanent record?			
Is service maintenance by contract?			
Is preventative maintenance a[illegible]			
Is a permanent service record [illegible] in a logbook?			
Has the instrument been modified in any way?			
Is the instrument properly vented and are appropriate traps in place?			
Is a glass jet separator in place and operational?			
Is an electronic data storage service available?			
Is a split/splitless capillary injector in place?			
Is the column direct to the source?			
Is the EPA/NIH mass spectral library search system current?			

IV. Sample Analysis Instrumentations

A. /DS Instrumentation

	Manufacturer	Model	Installation Date
GC/MS ID #			
GC/MS ID #			
GC/MS ID #			
Data System ID #			
Data System ID #			
Purge and Trap ID #			
Purge and Trap ID #			

COMMENTS ON GC/MS/DS INSTRUMENTATION:

B. GC Instrumentation

	Manufacturer	Model	Installation Date	Detector(s)
GC ID #				
GC ID #				
Data System ID #				
Purge and Trap ID #				

ITEM	YES	NO	COMMENT
Are manufacturer's operating manuals readily available to the operator?			
Is there a calibration protocol in use by the operator?			
Are calibration results kept in a permanent record?			
Is service maintenance by contract?			
Is preventative maintenance applied?			

A. GC/MS/DS Instrumentation

ITEM	YES	NO	COMMENT
Is there evidence that at least one GC/MS/DS system can be reasonably expected to be operating acceptably at a given time?			
Are extensive in-house replacement parts available?			

SATISFACTORY? ☐ ☐

Comments on GC/MS Instrumentation

V. Data Handling and Review

ITEM	YES	NO	COMMENT
Data calculations spot-checked by a second person?			
Is any corrective action that has been taken on reported data?			
Have standard curves been adequately documented?			
Are in-house control charts maintained for analysis (e.g., internal standard control charts)?			
Do QC records show corrective action when analytical results fail to meet criteria?			
Do supervisory personnel review the data and QC results?			

B. G C Instrumentation

ITEM	YES	NO	COMMENT
[illegible] a [illegible]anent service record maintained in a logboo[illegible]			
Ha[illegible] [illegible]trume[illegible]en modified in any way?			
Is tha ins[illegible] properly vented or are appropriat[illegible]s f[illegible]			
Ie there evide[illegible]at at le[illegible]ne GC syetem can be reasona[illegible]xpected [illegible] operating acceptably at [illegible]iven time[illegible]			
Are in-house replacement part[illegible]?			

[illegible]TISFA[illegible] ☐ ☐

Comments nn GC Instrumentetion

VI. Quality Control Manual Checklist

ITEM	YES	NO	COMMENT
Does the laboratory maintain a Quality Control Manual?			
Does the manual address the important elements of a QC program including the following:			
a. Personnel?			
b. Facilities and equipment?			
c. Operation of instruments?			
d. Documentation of procedures?			
e. Preventive maintenance?			
f. Reliability of data?			
g. Data validation?			
h. Feedback and corrective action?			
i. Instrument calibration?			

Additional Comments

VII SUMMARY

a. Summary Checksheet (Page 1 of 2)

ITEM	YES	NO	COMMENT
Do responses to the evaluation indicate that project and supervisory personnel are aware of QA/QC application to the project?			
Do project supervisory personnel place positive emphasis on QA/QC?			
Have responsibilities for QA/QC aspects of the project been open and direct?			
Has a cooperative attitude been displayed by all project and supervisory personnel?			
Does the organization place adequate emphasis on quality assurance?			
Have any QA/QC deficiencies been discussed before leaving?			
Is the overall quality assurance adequate to accomplish the objectives of the project?			
Have corrective actions recommended during previous evaluations been implemented? If not provided details in Section VII.b.			

b. Additional Comments (Page 2 of 2)

B. GC Instrumentation

ITEM	YES	NO	COMMENT
[illegible] service record maintained in a logbo[illegible]			
H[illegible] been modified in any way?			
Is the in[illegible] properly vented or are appropriat[illegible]ps in[illegible]?			
Is there evide[illegible]hat at l[illegible] one GC system can be reason[illegible] expected [illegible]e operating acceptably at [illegible] given tim[illegible]			
Are in-house replace[illegible]t par[illegible]le?			

ATISFA[illegible]Y? ☐ ☐

Comments on GC Instrumentation

V. Data Handling and Review

ITEM	YES	NO	COMMENT
[illegible]ta c[illegible]lations spot-checked by a second [illegible]			
D[illegible] corrective action that has b[illegible]ed data?			
Have stan[illegible]rves been adequately documented?			
Are in-ho[illegible] c[illegible] cont[illegible] charts maintained for analysis [illegible] interna[illegible]ndard control charts)?			
Do QC records s[illegible]rectiv[illegible] when analytical results [illegible] to [illegible]teria?			
Do supervisory person[illegible] rev[illegible] he[illegible]a and QC results?			

A. GC/MS/DS Instrumentation

ITEM	YES	NO	COMMENT
Is there evidence that at least one GC/MS/DS system can be reasonably expected to be operating acceptably at a given time?			
Are adequate in-house replacement parts available?			

SATISFACTORY? ☐ ☐

Comments on GC/MS Instrumentation:

B. GC Instrumentation

	Manufacturer	Model	Installation Date	Detector(s)
GC ID				
GC ID #				
Data System ID #				
Purge and Trap ID #				

ITEM	YES	NO	COMMENT
Are manufacturer's operating ma[illegible] readily available to the operator?			
Is there a calibration protocol in use by operator?			
Are calibration results kept in a permanent record?			
Is service maintenance by contract?			
Is preventative maintenance applied?			

IV. Sample Analysis Instrumentations

A. GC/MS/DS Instrumentation

	Manufacturer	Model	Installation Date
GC/MS ID #			
GC/MS ID #			
GC/MS ID #			
Data System ID #			
Data System ID #			
Purge and Trap ID #			
Purge and Trap ID #			

COMMENTS ON GC/MS/DS INSTRUMENTATION:

A. GC/MS/DS Instrumentation

ITEM	YES	NO	COMMENT
[illegible]facturer's operating manuals readily available to the operator?			
I[illegible]on protocol in use by the op[illegible]			
Are calib[illegible] results kept in a permanent record?			
Is service ma[illegible]tance by [illegible]act?			
Is preventative [illegible]nance s[illegible]?			
Is a permanent service [illegible]nt[illegible] in a logbook?			
Has the instrument been [illegible] in [illegible]			
Is the instrument properly ve[illegible] are appropriate traps in place?			
Is a glass jet separator in place a[illegible] operational?			
Is an electronic data storage service availab[illegible]			
Is a split/splitless capillary injector in place?			
Is the column direct to the source?			
Is the EPA/NIH mass spectral library search system current?			

III. Sample Preparation Area (Continued)

ITEM	YES	NO	COMMENT
[illegible] laboratory supervisor document that trace[illegible] water is available for preparation of standards and blanks?			
Is [illegible]lytical balance located away from draft and area[illegible] to rapid temperature changes?			
Has the b[illegible] been [illegible]ed within one year by a certi[illegible]			
Is the balance routinely ch[illegible]d with class S weights before [illegible]use and the results recorded in a logbook?			
Are the solvent storag[illegible] properly vented in order to prevent po[illegible] contaminated?			
Is the appropriate portion of the S[illegible]dable to the analyst at the sample pr[illegible] area?			
Are reagent grade or higher purity ch[illegible] used to prepare standards?			
Are fresh analytical standards prepare[illegible] frequency consistent with good QA?			
Are reference materials properly labeled wi[illegible] concentrations, date of preparation, and the identity of the person preparing the sample?			
Is a standards preparation and tracking logbook maintained?			

III. Sample Preparation Area (Continued)

ITEM	YES	NO	COMMENT
[illegible] record bench data in a neat and accu[illegible] manner?			
Are [illegible] separately from sample [illegible]			
Is the SO[illegible] glassware washing posted at the cleaning s[illegible]?			
Is the temp[illegible]t the r[illegible] gerations/freezer recorded daily[illegible]			

Additional Comment[illegible]

II. Sample Receipt and Storage Area (Continued)

ITEM	YES	NO	COMMENT
[illegible] receipt/storage and temperature [illegible] maintained in a manner consistent with CLP?			
[illegible] of the individual maintaining the notebook [illegible] examined and reviewed the notebook [illegible] periodically, and signed his/her name there [illegible] together with the date and appropriate comments as to whether or not the notebook [illegible] in an appropriate manner.			

Additional Comments:

III. Sample Preparation Area

[illegible] ouring the facilities, give special attention to: (a) the over[illegible]rance of organization and neatness, (b) the proper maintenance of f[illegible] instrumentation, (c) the general adequacy of the facilities to [illegible]sh t[illegible]equired work.

ITEM	YES	NO	COMMENT
Is the [illegible]orat[illegible]aintained in a clean and organize[illegible]			
Does the [illegible]ate[illegible]o have adequate workspace [illegible]20 [illegible], linear feet of unencumbered [illegible]space pe[illegible]nalyst)?			
Are the toxic [illegible]ical handling areas either a stainless steel [illegible]or an i[illegible]ous material covered with absor[illegible]ater[illegible]			
Are contamination-free [illegible]reas [illegible]or trace level analytical work?			
Are contamination-free work areas [illegible] for the handling of toxic materials [illegible]ove h[illegible]?			
Are exhaust hoods provided to allow contamination-free work with volat[illegible]te[illegible]			
Is the air flow of the hoods periodica[illegible] checked and recorded?			
Are chemical waste disposal policies/proce[illegible] adequate?			
Does the laboratory have a source of distilled/ demineralized water?			
Is the conductivity of distilled/demineralized water routinely checked and recorded?			

I ORGANIZATION AND PERSONNEL (Page 2 of 2)

ITEM	YES	NO	COMMENT
Do personnel assigned to this project have the appropriate level and type of experience to successfully accomplish the objectives of this project?			
Is the organization adequately staffed to meet project commitments in a timely manner?			
Was the Quality Assurance Officer available during the evaluation? Name: _____			
Does the laboratory Quality Assurance Officer report to senior management level?			
Was the Project Manager available during the evaluation?			

Additional Comments

II. Sample Receipt and Storage Area

ITEM	YES	NO	COMMENT
Is a sample custodian designated? If yes, name the sample custodian. Name: _____			
Are written Standard Operating Procedures (SOP) developed for receipt and storage of samples?			
Is the appropriate section of the SOP available to the analyst in the sample receipt/storage area?			
Are the sample shipping containers opened in a manner which prevents possible laboratory contamination?			
Are samples that require preservation stored in such a way as to maintain the preservation?			
Are volatile samples stored separately from semi-volatile samples?			
Are adequate facilities provided for storage of samples, including cold storage?			
Is the temperature of the cold storage recorded daily in a logbook?			

ORGANIC LABORATORY EVALUATION CHECKSHEET

Laboratory: _____

Date: _____

Type of Evaluation: _____

Contract Number: _____

Contract Title: _____

Personnel Interviewed:

Name	Title

Laboratory Evaluation Team:

Name	

ZAT[illegible]AND PERSONNEL (page 1 of 2)

[illegible]M	YES	NO	COMMENT
L[illegible] or [illegible]ct Manager (individual respons[illegible]verall technical effort): Name: _____			
GC/MS Operato[illegible] Name: _____ Experience: 9 [illegible]inimu[illegible]rement			
GC/MS Spectral Interp[illegible]io[illegible]per[illegible] Name: _____ Experience: 2 years [illegible]equire[illegible]			
Purge and Trap Expert: Name: _____ Experience: 6 months minimum req[illegible]			
Extraction Concentration Expert: Name: _____ Experience: 1 year minimum requirement			
Pesticide Residue Analysis Expert: Name: _____ Experience: 2 years minimum requirement			

EVENT SEQUENCE FOR PRE-AWARD SITE EVALUATION

I. Meeting with Laboratory Manager and Project Manager

General discussion of purpose of site visit, purpose of analyses and current contract award status.

II. Verification of Personnel

Review qualifications of contractor personnel in place and committed to project.

III. Verification of Instrumentation

Review equipment in place and committed to project. The bidder must demonstrate adequate equipment redundancy, as defined in the Laboratory Evaluation Checksheet, to ensure capability to perform required analyses in the required time.

IV. Quality Control Procedures

Walk through laboratory to review:

1. Sample receiving and logging procedures.
2. Sample and extract storage area.
3. Procedures to prevent sample contamination.
4. Security procedure for laboratory and samples.
5. Safety procedures.
6. Conformance to written SOPs.
7. Instrument records and logbooks.
8. Sample and data control systems.
9. Procedures for handling and disposing of hazardous materials.
10. Glassware cleaning procedures.
11. Status of equipment and its availability.
12. Technical and managerial review of laboratory operation and data package preparation.
13. Procedures for data handling, analysis, reporting and case file preparation.
14. Chain-of-custody procedures.

V. Identification of Needed Corrective Actions

Discuss with Project Manager the actions needed to correct weaknesses identified during site inspection, PE sample analysis or production of reports (hard copies and magnetic tapes) and documentation. Determine how and when corrective actions will be documented, how and when improvements will be demonstrated, and the contractor employee responsible for corrective actions.

Figure 2. Event Sequence for Pre-Award Site Evaluation.

VI. Review of Standard Operating Procedures (SOPs)

Review SOPs with Project Manager to assure that the laboratory understands the dimensions and requirements of the program.

Figure 2. (Continued).

Part 2 - Evaluation of Bidder-Supplied Documentation

At the time of submission of PE sample data results, the bidder shall submit documented evidence that it has the personnel, equipment and internal procedures in place for successful performance of contract requirements. Documentation shall include at a minimum:

1. Functional descriptions of key personnel.

2. Detailed resumes of key personnel, including previous work experience and publications.

3. Inventory of laboratory capital equipment, indicating which items of equipment will be assigned for use in this contract.

4. Inventory of general analytical support equipment, such as glassware, water baths.

5. Description of laboratory space allocated for this contract, including dimensions and relative proximities of each area.

6. Standard Operating Procedures (SOPs) for:

   a. Sample receipt, handling storage and control.

   b. Security, chain-of-custody and document control.

   c. Sample analysis, including types of analysis required herein.

   d. Traceability of calibration standards.

   e. Ongoing or routine laboratory operations, including copies of representative pages from recent instrument and maintenance logs.

   f. Laboratory safety

   g. Laboratory QA/QC including procedures for in-house technical and managerial review of laboratory operations and data package preparation.

   f. Data production, reduction, transcription, verification, review, distribution and in-house storage.

   g. Reporting status of all samples in-house on an interim basis (i.e., daily, weekly, monthly).

   h. Waste handling/disposal procedures.

The bidder shall note that 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 bidder's ability to successfully fulfill all contract requirements.

The bidder shall submit copies of the required documentation (items 1-6, above) at the same time that PE sample data are submitted to the Government evaluator (see Part 1 of this section). Documentation will not be accepted if submitted at any other time. Submitted documentation will be reviewed by EPA, and verification of the use of documented procedures in the laboratory will be part of the laboratory site evaluation (see Part 3, following).

Part 3 - Laboratory Site Evaluation

When a laboratory has successfully demonstrated the ability to analyze PE samples and report data acceptably and when EPA has reviewed bidder-supplied documentation (see Part 2), the laboratory may be subjected to a pre-award site evaluation. The purpose of this evaluation is primarily to verify the laboratory's claims as represented in the bid and supplied documentation. However, it also serves as a mechanism for performing several important secondary functions. These include:

- presentation of project goals,
- discussion of weaknesses identified through the PE sample analysis,
- identification of correctable weaknesses in the laboratory facility, and
- establishment of a baseline for further laboratory audits (Evidence and QA/QC).

The following event sequence (Figure 2) describes the protocol which will generally be employed by the Government during a site evaluation. The Government reserves the right to deviate from the sequence of events described herein should circumstances warrant such deviation. Any such determination to deviate will be made by the Contracting Officer.

Following the event sequence is an example of the Laboratory Evaluation Checksheet (Figure 3) which will be filled out by the Government. A similar Laboratory Evaluation checksheet will be used by the Government during future evaluations of contractors, in order to maintain a continuous evaluation record.

	A	B
Chromatograms for pesticide fraction of samples, standards, blanks, matrix spikes, duplicates. All chromatograms must be clearly labeled. Peak area reports must be included. Compounds identified must be labeled on each chromatogram.	____	____
Spectra (deduct 1 point each)		
1. Mass spectra submitted for all compounds identified (both HSL and non-HSL) in samples and standards.	____	____
2. Both reconstructed and background subtracted spectra submitted for all HSL compounds identified in C. above.	____	____
3. Spectra for all compounds identified and labeled appropriately.	____	____
D. Contractual Forms filled out correctly (deduct 2 points each)		
1. Organic Analysis Data Sheet (Form I) for samples, blanks, matrix spikes, and matrix spike duplicates filled out completely and correctly (each parameter sheet followed by a concentration or qualifier).	____	____
2. Tentatively Identified Compounds (Form I Part B) filled out completely and correctly for samples and reagent blanks if non found.	____	____
3. Surrogate Percent Recovery Summary Form fully and correctly filled out for surrogates in samples, blanks, matrix spikes, and matrix spike duplicates. Properly completed form for each sample matrix.	____	____
4. Matrix Spike/Matrix Spike Duplicate Summary (Form III) completely and correctly filled out.	____	____

Figure 1. (Continued).

Reagent Blank Summary (Form IV) completely and correctly filled out.	____	____
6. GC/MS Tuning and Mass Calibration (Form V) completely and correctly filled out for each instrument and for every 12-hour period samples were analyzed (DFTPP and BFB).	____	____
Initial Calibration Data (Form VI) completely and correctly filled out for the BNA fraction and the BNA fraction.	____	____
8. Continuing Calibration Data (Form VII) completely and correctly filled out for the [illegible] fraction and/or the BNA fraction at the required frequency.	____	____
9. Pesticide/PCB Evaluation Standards Summary (Form [illegible]) completely and correctly filled out for each 24-hour period for each GC column used to analyze samples.	____	____
10. Pesticide/PCB [illegible] Summary (Form IX) completely and correctly filled out for each 12-hour period for each GC column used to analyze samples.	____	____
11. Pesticide/PCB Identification Form X completely and correctly filled out.	____	____
TOTAL SCORE FOR SECTION V	50	50
COMBINED SCORE FOR SECTION V	____	____
PERCENT SCORE FOR SECTION V	____	____

NOTE: Only 60 percent of a score will be awarded for:

- submission of only the raw data, even though a value within criteria when computed by the evaluator,
- use of an incorrect equation resulting in an incorrect value even though when recalculated by the evaluator, the value is within criteria, and
- errors due to computational mistakes or improper use of significant figures or improper rounding off procedures, even though the value is within criteria when recomputed by the evaluator.

Figure 1.

	A	B
IV ... ssurance Data (... imu... 100 points each sample)		
A. ...rrogate Spikes Percent Recovery (...aximum = 45 points each sample)		
...ate spike percent recovery for ...ne or more required surrogate co... outside of contractual windows ...reagent blank analysis, deduct 10 ...s each.	___	___
2. ... percent recovery ...or ...e or m... required surrogate com...d outside ...contractual windows in ...mple, ded... points each.	___	___
3. Failu... perform ... submit surrogate spike p... reco... any blank, sample, matri... sp... ...ix spike duplicate, d... t ...in...	___	___
B. Reagent Blank Ana... (Maximum = 45 poin... ...ample...)		
1. For each HSL compound ... in th... reagent blank at gr... ...n the ...act Required Detection L... (CRD...) ... 5 points each.	___	___
2. For each non-HSL compoun... th... ...ent blank at greater than 10% of t... internal standard area free ... deduct 5 points each.	___	___
3. Failure to perform or submit a re... ...ank analysis at the required frequenc... ...duct 25 points each.	___	___

Figure 1. (Continued).

	A	B
Matrix Spike/Matrix Spike Duplicate (Maximum = 10 points each sample)		
For each matrix spike or matrix spike duplicate, HSL compound with a percent recovery outside the acceptance window set by EPA, deduct 1/2 point each.	____	____
2. For each HSL compound in the matrix spike/matrix spike duplicate with a relative percent difference (RPD) outside the window set by EPA, deduct 1/2 point each.	____	____
TOTAL SCORE FOR SECTIONS III AND IV	250	250
COMBINED SCORE FOR SECTIONS III AND IV	____	____
PERCENT SCORE FOR SECTIONS III AND IV	____	____

V. Reporting and Delivery
(Maximum = 50 points each sample)

	A	B
A. DFTPP and BFB (deduct 1 point)		
1. Mass listing and bar graph output submitted for each instrument used in 12-hour period samples were analyzed	____	____
B. RICs and Chromatograms (deduct 1 point)		
1. RICs for each fraction of samples, standards, blanks, matrix spikes, and duplicates	____	____
2. RICs normalized to largest non-solvent peak	____	____
3. Surrogates and internal standards labeled on RIC.	____	
4. Quantitation/Identification data system reports submitted with all RICs.	____	____

Figure 1. (Continued).

	A	B
B. Initial Calibration of the GC/MS System (Maximum = 40 points each sample)		
1. Initial calibration data for VOA or BNA with one or more System Performance Check Compound (SPCC) average response factor (RF) less than 0.300 for VOA fraction or less than 0.050 for BNA fraction, deduct 5 points for each.	____	____
2. Initial calibration data for VOA or BNA with one or more Calibration Check Compound percent relative standard deviation (%RSD) greater than 30%, deduct 5 points for each.	____	____
C. 24-Hour Standard Evaluation Requirements for GC/EC (Maximum of 40 points each sample)		
1. Linearity for Aldrin, Endrin, 4,4-DDT or Dibutylchlorendate in Evaluation Mixtures A, B, and C exceeds 30% Relative Standard Deviation (%RSD), deduct 3 points each.	____	____
2. The percent breakdown for Endrin exceeds 10% or 5% for 4,4-DDT in Evaluation Mix B deduct 3 points	____	____
3. The retention time shift for Dibutylchlorendate exceeds a 2% difference for packed columns (0.3% difference for capillary columns) between the initial standard calibration (Mix A) and Evaluation Mixtures B and C, Individual Standards Mixtures A or B and all other pesticide/PCBs analyzed during the 24-hour, deduct 2 points each.	____	____
4. Failure to perform linearity check standards analysis on all GC columns utilized for sample analysis, deduct 10 points each.	____	____
5. Failure to perform linearity, breakdown and/or standards analysis at required 24-hour frequency, deduct 10 points each.	____	____

Figure 1. (Continued).

A = B =

D. ...uing Calibration of the GC/MS System
(Ma...m = 15 points each sample)

1. Continuing calibration data for VOA or BNA with ...stem Performance Check Compounds ...lly response factor (RF) less than ... VOA fraction or less than 0.050 ... for ... fraction, deduct 1 point each. ____ ____

2. ...ing calibration data for VOA or BNA ...Calibration Check Compounds with percent ...er... greater then 25%, deduct 5 ... ____ ____

3. Fai... to perfo... continuing calibration ana... at the ...red 12-hour frequency, dedu... points. ____ ____

E. 12-Hour Calibrati... Re... for GC/EC
(Maximum = 15 po... e... am...

1. The Calibrat... Fac... or ... individual standard exce... ifferen... for a quantitation ru... eeds ... difference for a confirmation run du... 2-hour period, deduct 2 point... ____ ____

2. The percent breakdown ... End... 10% or 5% for 4,4'-DDT in ... B during a 12-hour period, ... s each. ____ ____

3. The retention shift for Dibu... exceeds a 2% difference for p... GC columns (0.3% difference for capill... column) between the initial stand... (Evaluation Mix A) and any sample ...yzed during a 12-hour period, deduct 2 points each. ____

4. Failure to perform analysis of Evaluation Mix B or Individual Mixes A or B at the required frequency, deduct 15 points. ____ ____

Figure 1. (Continued).

PREAWARD PERFORMANCE EVALUATION SAMPLE DATA SCORING

Laborato[illegible] _____

[illegible] _____ Date _____

SUMMARY: [illegible]AXIMUM SCORE FOR SECTIONS I - V _____

[illegible]OR SECTIONS I - V _____

[illegible]RE FOR SECTIONS I - V _____

I. Hazardo[illegible]ost[illegible] (HSL) Results (Maximum = 105 points each sample)

A. Iden[illegible]s (Max[illegible] = 40 points each sample) A B

[Number [illegible] compounds [illegible] identified (_____) X 40/numbe[illegible] compounds[illegible]n study (_____) = (_____) p[illegible]educted] _____ _____

B. Confirmations

[Number of pesti[illegible]s/P[illegible]no[illegible]firmed by GC/MS with appropriate [illegible]al e[illegible]ct [illegible]ncentration (_____) X 40/number of pe[illegible]Bs app[illegible]ate for GC/MS confirmation in stu[illegible]) = [illegible] points deducted] _____ _____

C. Quantitation (Maximum = [illegible]s each[illegible]e)

[Number of compounds not withi[illegible] criteria (_____) X 40/number [illegible]po[illegible]n study (_____) = (_____) point[illegible]educ[illegible] _____ _____

D. HSL False Positive Identificatio[illegible] Required Detection Limits (Maximum = 25 points each sample)

[Number of false positives (_____) X 2[illegible]ber of compounds in study (_____) = (_____) poin[illegible] deducted] _____

Figure 1. Preaward Performance Evaluation Sampl[illegible]a Scorin[illegible]

	A	B
II. Non-[illegible] sults (Maximum = 45 points each sample)		
[illegible]ent[illegible]rations (Maximum = 30 points each sample)		
[illegible]mber of non-HSL's not identified (____) X [illegible] number of compounds in study (____) = (____) [illegible] deducted]	____	____
B[illegible] HSL Fa[illegible]ositive Identifications (M[illegible]n[illegible] points each sample)		
[Numb[illegible] false positives (____) X 15/number of c[illegible]s [illegible] (____) = (____) points dedu[illegible]	____	____
TOTAL SC[illegible]OR SECTIO[illegible] AND II	150	150
COMBINED S[illegible] SECTIONS [illegible] AND II	____	____
PERCENT SCORE FOR SECTIO[illegible] I	____	____

	A	B
III. Tuning and Calibratio[illegible]a (Maximum = 150 points [illegible]n sa[illegible])		
A. GC/MS Tuning and Mas[illegible]tion (Maximum = 40 points e[illegible]sampl[illegible]		
1. For each DFTPP perfor[illegible]e wi[illegible] ion abundance ratios o[illegible]e cri[illegible] deduct 10 points.	____	____
2. For each BFB performance t[illegible] wit[illegible] ion abundance ratios outside cri[illegible] deduct 10 points.	____	____
3. Failure to perform a DFTPP or BF[illegible] performance tune at the required 1[illegible] frequency, deduct 10 points.	____	____

Figure 1. (Continued).

WA 85-J176
WA 85-J177
WA 85-J178

ATTACHMENT B

PRE-AWARD BID CONFIRMATION

It is of the utmost importance that reliable results be obtained from sample analyses performed under this contract since these results will be used to support enforcement actions against alleged offenders. Hence, it is vital that bidder capability be clearly determined prior to contract award.

CONSIDERATION IN DETERMINATION OF BIDDER RESPONSIBILITY

To demonstrate that the bidder laboratory has, in place and operating, all the personnel, equipment and internal standard procedures needed for performance of contract requirements, requires three steps:

1. Bidder's analysis of EPA-provided Performance Evaluation (PE) samples,

2. Bidder's submission of written standard operating procedures (SOPs), facility and equipment inventories, and position descriptions and staff resumes, and

3. Site evaluation of bidder's laboratory facility by Agency officials and/or Agency representatives.

The results of the PE sample analyses, evaluation of the bidder-supplied documentation, and the laboratory site evaluation will be considered by the Government in determining bidder responsiveness/responsibility, along with other pertinent factors which provide demonstration of the bidder's ability to perform the full scope of the contract requirements. These other factors of consideration include, but are not limited to:

* Demonstrated experience of bidder in analyzing hazardous substances by contract-stipulated GC/MS methodology;

* Performance of bidder on other Program analytical contracts (previous or current);

* Demonstrated ability of bidder to consistently perform volume analysis at the contract-stipulated monthly sample capacity;

* Current laboratory loadings impact on ability to perform (in terms of attaining optimum distribution of program workload); and

* Effect on potential laboratory performance of overall laboratory organization and management structure, adherence to Good Laboratory Practices and organization of workflow.

Any and/or all of the factors described herein may be considered by the Government in determining the responsibility of the bidder for purposes of contract award under this solicitation.

Part 1 - Performance Evaluation Sample Analysis

Prior to award, the bidder must demonstrate its ability to perform the requirement by analyzing and documenting the results for one to three sets of unknown Performance Evaluation (PE) samples. The purpose of this analysis is to provide evidence that the laboratory personnel involved fully understand the required analytical methods and that these methods can be performed satisfactorily by laboratory personnel using their equipment. Furthermore, it provides evidence that they understand the documentation and reporting requirements of the contract.

The PE samples are designed to test the capability of laboratories to perform the full set of contract requirements which include, but are not limited to:

- Identification of hazardous substances
- Quantitation of identified hazardous substances
- Reproducibility of analytical data
- Accuracy of analytical data (percent recovery)
- Ability to maintain a contamination-free environment
- Ability to perform mass spectral library searches
- Understanding of documentation requirements
- Understanding of reporting requirements

The laboratory shall analyze one to three sets of PE samples during the evaluation. Analysis and reporting requirements of the project shall be completed within twenty-one (21) calendar days from receipt of samples at the laboratory at the following address: USEPA EMSL-LV, Attn: J. Gareth Pearson, Chief, Toxics and Hazardous Waste Operations Branch, 944 East Harmon Avenue, Las Vegas, NV 89109. Upon request by the Contracting Officer, the magnetic raw data tape shall be made available for Government review.

The evaluator will inspect the data and reports for compliance with the acceptance criteria set by EPA and use the elements and weighing similar to those in Figure 1 to score the results. A summary score (point, percent) will be derived once scores have been assigned to all sections. A summary report of comparative performance by all bidders will be prepared by the EMSL-LV and delivered to the Contracting Officer. The total points may be adjusted by the Government for all bidders in an impartial and equitable manner should it become necessary due to unanticipated difficulties with the PE samples.

CHAIN OF CUSTODY RECORD

PROJECT NAME

SAMPLERS (Signature)

STA. NO	DATE	TIME	COMP	GRAB	STATION LOCATION	NO OF CONTAINERS							REMARKS

Relinquished by (Signature)	Date / Time	Received by (Signature)	Relinquished by (Signature)	Date / Time	Received by (Signature)
Relinquished by (Signature)	Date / Time	Received by (Signature)	Relinquished by (Signature)	Date / Time	Received by (Signature)
Relinquished by (Signature)	Date / Time	Received for Laboratory by (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment, Copy to Coordinator Field Files

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Chain-of-Custody Record

Figure 4. Example Document Inventory Form for Each Case

1. Study plans or project plans.

2. Sample traffic records, weekly reports.

3. Custody records, sample tags, sample logs.

4. Laboratory logbooks, personal logbooks, instrument logbooks.

5. Laboratory data (sorted by sample), calibration and quality control results.

6. Data summaries and reports.

7. All other documents, forms or records referencing the samples.

Case # - Region - Serialized number

For example - 75-2-0240

All documents relevant to each case including: loghook pages, bench sheets, mass spectra, chromatograms, custody records, library search results, etc., are inventoried. Each data generator (analyst) is responsible for ensuring that all documents generated are placed in the file for inventory and returned to EPA. Figure 4 is an example of a document inventory.

Confidential Information

Any samples or information received with a request of confidentiality is handled as "confidential". A separate, locked file is maintained and segregated from other nonconfidential information. Data generated from confidential samples is treated as "confidential". Upon receipt of confidential information, the DCO* logs these documents into a Confidential Inventory Log. The information is then made available to authorized personnel, but only after it has been signed out to that person by the DCO. The documents shall be returned to the locked file at the conclusion of each working day. Confidential information may not be reproduced except upon approval by and under the supervision of the DCO. Any reproduction must be kept to an absolute minimum. The DCO will enter all copies into the document control system and apply the same requirements as the original. In addition, this inforamtion may not be destroyed except upon approval by and under the supervision of the EPA program manager and EPA Contracting Officer. The DCO shall remove and retain the cover page of any confidential information disposed of after one year and shall keep a record of the destruction in the Confidential Inventory Log.

*DCO is a document control officer assigned by the contractor to maintain control of confidential information.

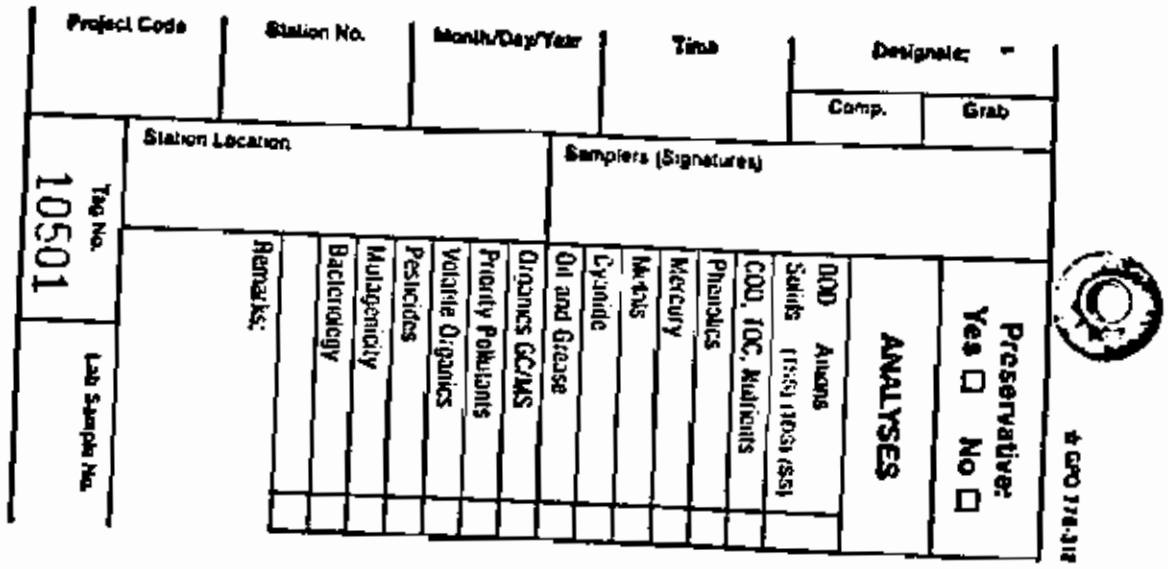

Figure 1. Example sample tag.

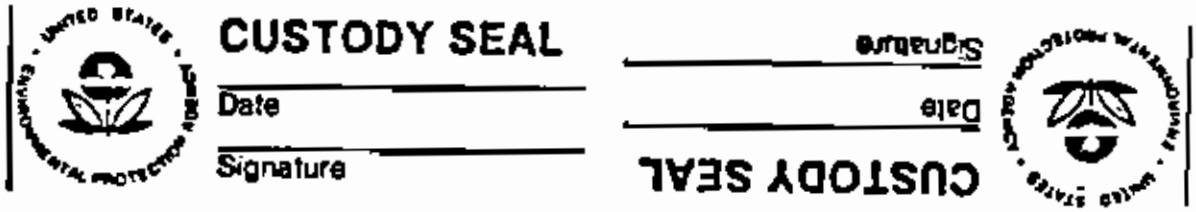

Figure 3. Example custody seal made of perforated paper stock.

Hazardous Waste Disposal Site
Contract Analytical Support
Chain-of-Custody and Document Control Procedures

Sample Control

A sample is physical evidence collected from a facility or from the environment. An essential part of this investigations effort is the control of the evidence gathered. To accomplish this, the following chain-of-custody and document control procedures have been established.

Sample Identification

Each sample bottle shall be labeled with a tag containing the sample number and sample description to identify the contents of the container. Additionally, the sample number shall be marked on the outside of any special packaging container to facilitate identification. Typical sample tags are shown in Figure 1.

Chain-of-Custody Procedures

Because of the nature of the data being collected, the possession of samples must be traceable from the time the samples are collected until they are introduced as evidence in legal proceedings. To maintain and document sample custody, the chain-of-custody procedures here must be followed.

A sample is under custody if:

1. It is in your actual possession, or
2. It is in your view, after being in your physical possession, or
3. It was in your possession and then you locked or sealed it up to prevent tampering, or
4. It is in a secure area.

To assure custody of samples during transport and shipping, each sample within a packing container is recorded on a chain-of-custody record shown in Figure 2. Each sample number is recorded and the number of containers shipped is recorded on the sheets. Also record the other information regarding the project, samples (or shipper if returning empty containers), method of shipment. The sheet must be signed and dated. The original custody sheet is then placed inside the package (protected from damage) and the package sealed. Sample containers, shipping boxes, coolers or other packages may be sealed by using the seal shown in Figure 3. The seal must be placed so the container cannot be opened without breaking the seal.

Upon receipt of samples in custody, inspect the package and note any damage to the sealing tape or custody seals. Note on the custody record or other logbook that the seals or locks were intact upon receipt if no tampering or damage appears to have occurred. Open the package and verify that each item listed on the sheet is present and correctly identified. If all data and samples are correct, sign and date the "received by Laboratory by" box. In the event errors are noted, record the discrepancies in the remarks column (initial and date each comment) then sign the chain-of-custody record. Report discrepancies to the Sample Management Office for remedies.

Laboratory Document Control

The goal of the Document Control Program is to assure that all documents for a specified case (group of samples) will be accounted for when the project is completed. The program includes a document numbering and inventory procedure for preparation of the specified documentation packages for each case.

Logbooks

All observations and results recorded by the laboratory but not on pre-printed data sheets are entered into permanent laboratory logbooks. Data recorded are referenced with the case number, date and analyst's signature at the top of the page. Data from only one case are recorded per page. When all the data from a case are compiled, copies of all logbook entries must be included in the documentation package.

Instrument logs are also limited to one case per page with the case number recorded at the top of each page. Copies of these logs must also be included in the final documentation package.

Corrections to Documentation

All documentation in logbooks and other documents shall be in ink. If an error is made in a logbook assigned to one individual, that person should make corrections simply by crossing a line through the error and entering the correct information. Changes made subsequently are dated and initialed. Corrections made to other data records or non-personal logbooks are made by crossing a single line through the error, entering the correct information and initialing and dating the correction.

Consistency of Documentation

Before releasing analytical results, the laboratory assembles and cross checks the information on sample tags, custody records, lab bench sheets, personal and instrument logs and other relevant data to ensure that data pertaining to each particular sample or case is consistent throughout the record.

Document Numbering and Inventory Procedure

In order to provide document accountability of the completed analysis records, each item in a case is inventoried and assigned a serialized number and an identifier associating it to the case and region.

NOTE

The Contractor shall not deviate from the procedures described herein without the prior written approval of the Contracting officer: Provided, that the Contracting Officer may ratify in writing such deviation and such ratification shall constitute the approval required herein.

Specifications for Chain-of-Custody and Document Control Procedures

The contractor must have written standard operating procedures (SOP's) for receipt of samples, maintenance of custody, tracking the analysis of samples and assembly of completed data. These procedures are necessary to ensure that analytical data collected under this contract are acceptable for use in EPA enforcement case preparations and litigation. The contractor's SOP's shall provide mechanisms and documentation to meet each of the following specifications and shall be used by EPA as the basis for laboratory evidence audits.

1. The contractor shall have a designated sample custodian responsible for receipt of samples.

2. The contractor shall have written SOPs for receiving and logging in of the samples. The procedures shall include documentation of the sample condition, maintenance of custody and sample security and documentation of verification of sample tag information against custody records.

3. The contractor shall have written SOPs for maintenance of the security of the samples after log in and shall demonstrate security of the sample storage and laboratory areas.

4. The contractor shall have written SOPs for tracking the work performed on any particular sample. The tracking system shall include standard data logging formats, logbook entry procedures and a means of controlling logbook pages, computer printouts, chromatograph tracings and other written or printed documents relevant to the samples. Logbooks, printed forms or other written documentation must be available to describe the work performed in each of the following stages of analysis:

   Sample receipt
   Sample extraction/preparation
   Sample analysis
   Data reduction
   Data reporting

5. The contractor shall have written SOPs for organization and assembly of all documents relating to each EPA case. Documents shall be filed on a case specific basis. The procedures must ensure that all documents including logbook pages, sample tracking records, measurement readout records, computer printouts, raw data summaries, correspondence and any other written documents having reference to the case are compiled in one location for submission to EPA. The system must include a document numbering and inventory procedure.

6. Document control and chain-of-custody records include but are not limited to: sample tags, custody records, sample tracking records, analysts logbook pages, bench sheets, measurement readout records, extraction and analysis chronicles, computer printouts, raw data summaries, instrument logbook pages, correspondence, and the document inventory.

EXHIBIT F

CHAIN-OF-CUSTODY AND DOCUMENT

CONTRDL PRDCEDURES

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VII SUMMARY

a. Summary Checksheet (Page 1 of 2)

ITEM	YES	NO	COMMENT
Do responses to the evaluation indicate that project and supervisory personnel are aware of QA/QC relation to the project?			
Do project supervisory personnel place positive emphasis on QA/QC?			
Have responsibilities for QA/QC aspects of the project been given and discussed?			
Has a cooperative attitude been displayed by all project and supervisory personnel?			
Does the organization place the appropriate emphasis on quality assurance?			
Have any QA/QC deficiencies been discussed before leaving?			
Is the overall quality assurance program adequate to accomplish the objectives of the project?			
Have corrective actions recommended during previous evaluations been implemented? If not provided details in Section VII.b.			

VI. Quality Control Manual Checklist

ITEM	YES	NO	COMMENT
Does the laboratory maintain a Quality Control Manual?			
Does the manual address the important elements of a QC program including the following:			
a. Personnel?			
b. Facilities and equipment?			
c. Operation of instruments?			
d. Documentation of procedures?			
e. Preventive maintenance?			
f. Reliability of data?			
g. Data validation?			
h. Feedback and corrective action?			
i. Instrument calibration?			

Additional Comments

b. Additional Comments (Page 2 of 2)