QUALITY ASSURANCE PROJECT PLAN
Addendum No. 1

MOSS-AMERICAN SITE
Milwaukee, Wisconsin

Phase I Remedial Investigation

WA 15.5LM7/Contract No. 68-W8-0040

August 18, 1989

GLT864/013.50

Remedial Planning Activities
(ARCS V)
Contract Number 68-W8-0040
QUALITY ASSURANCE PROJECT PLAN (QAPP)

Project Title: Moss-American Site
Milwaukee, Wisconsin
Phase I Remedial Investigation

EPA WA Nos.: 15-5LM7.0

EPA Project Officer: Stephen Nathan

Prepared By: CH2M HILL Date: August 18, 1989

Approved Jon Lash for _____ Date: 8/18/89
CH2M HILL Site Manager

Approved _____ Date: _____
CH2M HILL Program Manager

Approved _____ Date: _____
EPA Remedial Project Manager

Reviewed _____ Date: _____
EPA Director, Central Regional Laboratory

Approved _____ Date: _____
EPA QA Officer

GLT864/011.50

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GLT864/063.50

1.0 INTRODUCTION

The United States Environmental Protection Agency (EPA) requires participation of all U.S. EPA contractors in a centrally managed quality assurance (QA) program. This requirement applies to all environmental monitoring and measurement efforts mandated or supported by the EPA.

Each contractor generating data has the responsibility to implement minimum procedures to determine that the precision, accuracy, completeness and representativeness of its data are known and documented. Each U.S. EPA contractor must prepare a written Quality Assurance Project Plan (QAPP) covering each project it is contracted to perform.

This addendum revises portions of the Moss-American QAPP approved on October 15, 1987, so that it is consistent with Interim Work Plan Memorandum No. 1 for the Moss-American site that called for additional sediment sampling and lower detection level PAH analysis. The revisions are listed below in the same format as the approved QAPP. Where no changes are required, the QAPP section number is called out and the addendum text reads "No changes."

2.0 PROJECT DESCRIPTION

2.1 BACKGROUND

No changes.

2.2 PROJECT OBJECTIVES

The need for additional background sediment sampling was determined by the EPA, WDNR, and CH2M HILL during the site update meeting of November 15, 1988. The objective of the Additional Phase I RI sampling described in this addendum is to provide data necessary to establish background PAH compound concentrations in sediments in the Little Menomonee River upgradient of the site, in urban areas of the Little Menomonee River watershed and the Menomonee River watershed, and in similar urban settings.

Considerations of background concentrations is important at this site because the occurrence of PAH compounds is widespread in local sediments. Background data will be used to identify what portion of the PAHs found in sediments

downstream of the site is from site releases as compared with other sources and to establish reasonable remedial goals.

Additionally, trace levels of dioxin and its isomers have been detected on the site and in the Little Menomonee River sediments. Dioxin analyses will be performed on the background samples to determine background levels in this urban environment.

2.3 DATA USES AND DATA NEEDS

No changes.

2.4 DATA QUALITY OBJECTIVES

The data quality objectives to address the data needs and uses for the Moss-American RI activity covered by this addendum are:

1. To quantitatively define representative urban background concentrations for metals, semi-volatile organic compounds (SVOC) low-level PAHs, and dioxin in river sediments from the Little Menomonee River watershed and Menomonee River watershed

2. To quantitatively compare contaminant concentrations in Menomonee River sediments upstream and downstream of the confluence with the little Menomonee River

3. To support evaluation of remedial actions in the FS

4. To support establishment of remedial goals by the U.S. EPA

5. To support the U.S. EPAs selection of remedial alternatives from the FS

To meet these objectives, analytical methods must be capable of measuring low concentrations of PAH compounds. Actual concentrations are required to establish whether the 10^{-6} cancer risk identified for river sediment is due to site operations, background concentrations, or both. Therefore, the analytical level required to meet the Data Quality Objectives is Level 5.

Because PAHs are ubiquitous in most urban environments, it is possible that background concentrations exceed the 10^{-6} cancer risk concentrations determined for the river. Based on the trespass exposure scenario used in the risk

assessment for the Little Menomonee River, a 10^{-6} cancer risk is associated with concentrations of 600 to 700 µg/kg for each of 8 PAH compounds which are present in the sediment. To establish cleanup goals for consideration in the feasibility study, it is necessary to quantify PAH concentrations at levels at least 50 percent lower than the risk-based concentrations. Accurate and realistic cleanup goals are also necessary to establish an appropriate range for remedial actions to be evaluated during the feasibility study.

Detection limits obtained using RAS protocols during Phase I sediment sampling were typically 2,000 to 3,000 µg/kg or higher. These detection limits are higher than the contract required detection limits for soil because of the dry-weight correction factor and cleanup requirements of the RAS protocol, as well as sample dilution for contaminated samples. Special analytical services will, therefore, be required to satisfy the data quality objectives for PAH analysis.

Estimated concentrations of several PAH compounds in the relatively "cleaner" sediment samples collected during Phase I were on the order of several hundreds of µg/kg. Since background levels are probably equal to or less than these concentrations, a detection level of comparable or lower amount is appropriate.

A detection level of 100 µg/kg has been requested because it will allow quantification of individual PAH compounds at levels below RAS CRDL's even after dry-weight correction.

2.5 TARGET COMPOUND LIST

Known contaminants at the site include polycyclic aromatic hydrocarbons, dioxins, and other BNA compounds. Varying concentrations of several metals were also detected at the site. A list of the target analytes and required detection limits is presented in Appendix A, for the RAS metal and semivolatile organic analyses and in Appendix B for Special Analytical Services, (PAHs) and dioxins.

3.0 RI TASKS

3.1 PHASE I SUPPORT

No changes.

3.2 SOIL AND SEDIMENT SCREENING

No changes.

3.3 HYDROGEOLOGIC INVESTIGATIONS

No changes.

3.4 SURFACE WATER EVALUATION

No changes.

3.5 EVALUATION OF FIELD AND LABORATORY DATA

No changes.

3.6 COMMUNITY RELATIONS

No changes.

4.0 PROJECT ORGANIZATION AND RESPONSIBILITY

At the direction of the Region V Remedial Project Manager, with final authority by the Region V Remedial Project Officer, CH2M HILL has overall responsibility for all phases of the RI/FS. Quality Assurance and Quality Control are also provided by CH2M HILL. Figure 1 presents the project organization chart. Figure 2 presents the project schedule.

4.1 MANAGEMENT RESPONSIBILITIES

Project management will be conducted through CH2M HILL's regional office in Milwaukee. Contact will be maintained with the EPA's Remedial Project Manager (RPM) during all phases of the project.

Monthly reports will be submitted to keep the EPA apprised of the technical, financial, and schedule status of the project. Other CH2M HILL responsibilities include controlling budgets and schedules; selecting, coordinating, and scheduling staff and subcontractors for task assignments; and maintaining project quality control and assurance programs.

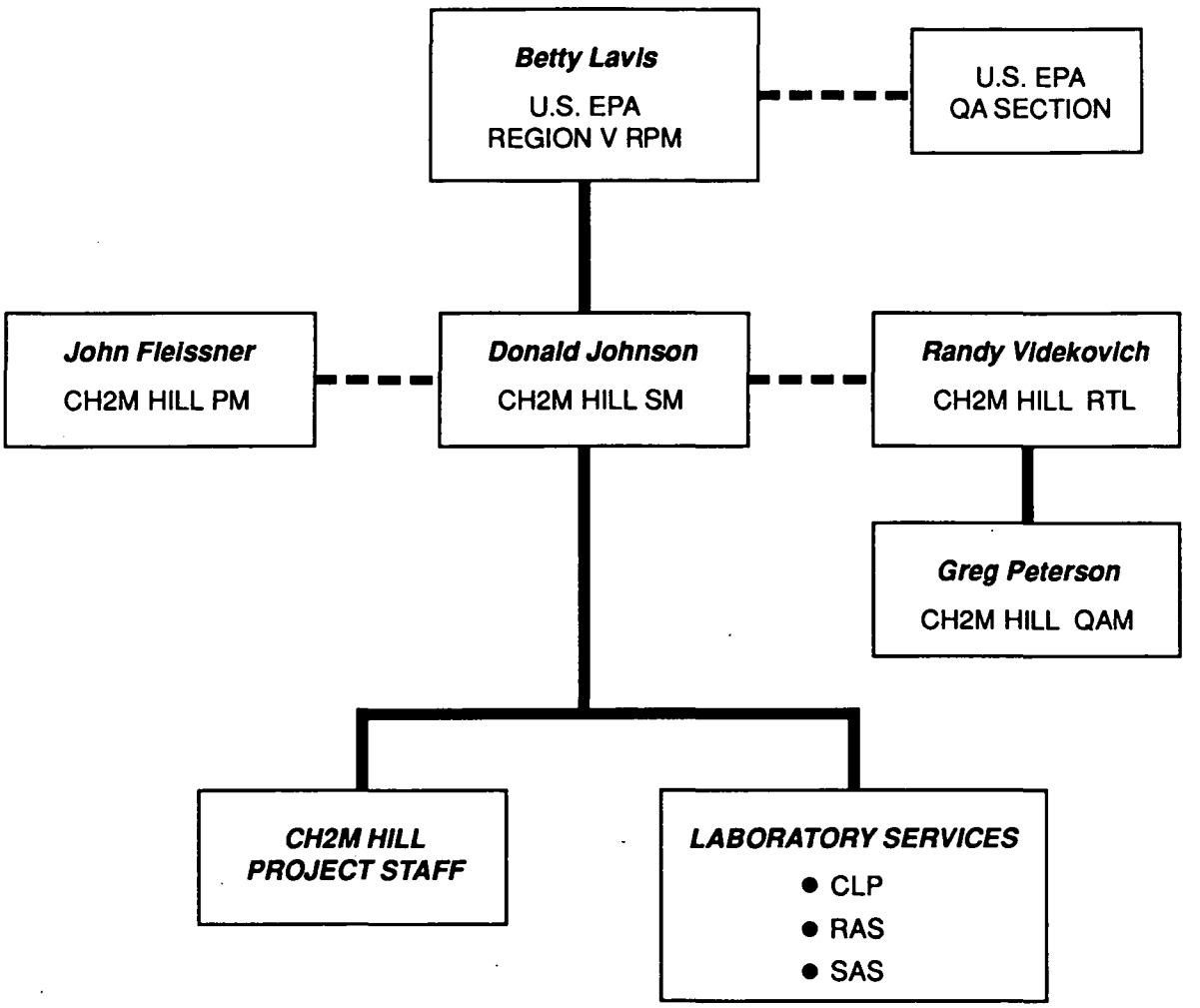

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FIGURE 1
PROJECT ORGANIZATION
MOSS-AMERICAN QAPP
ADDENDUM 1

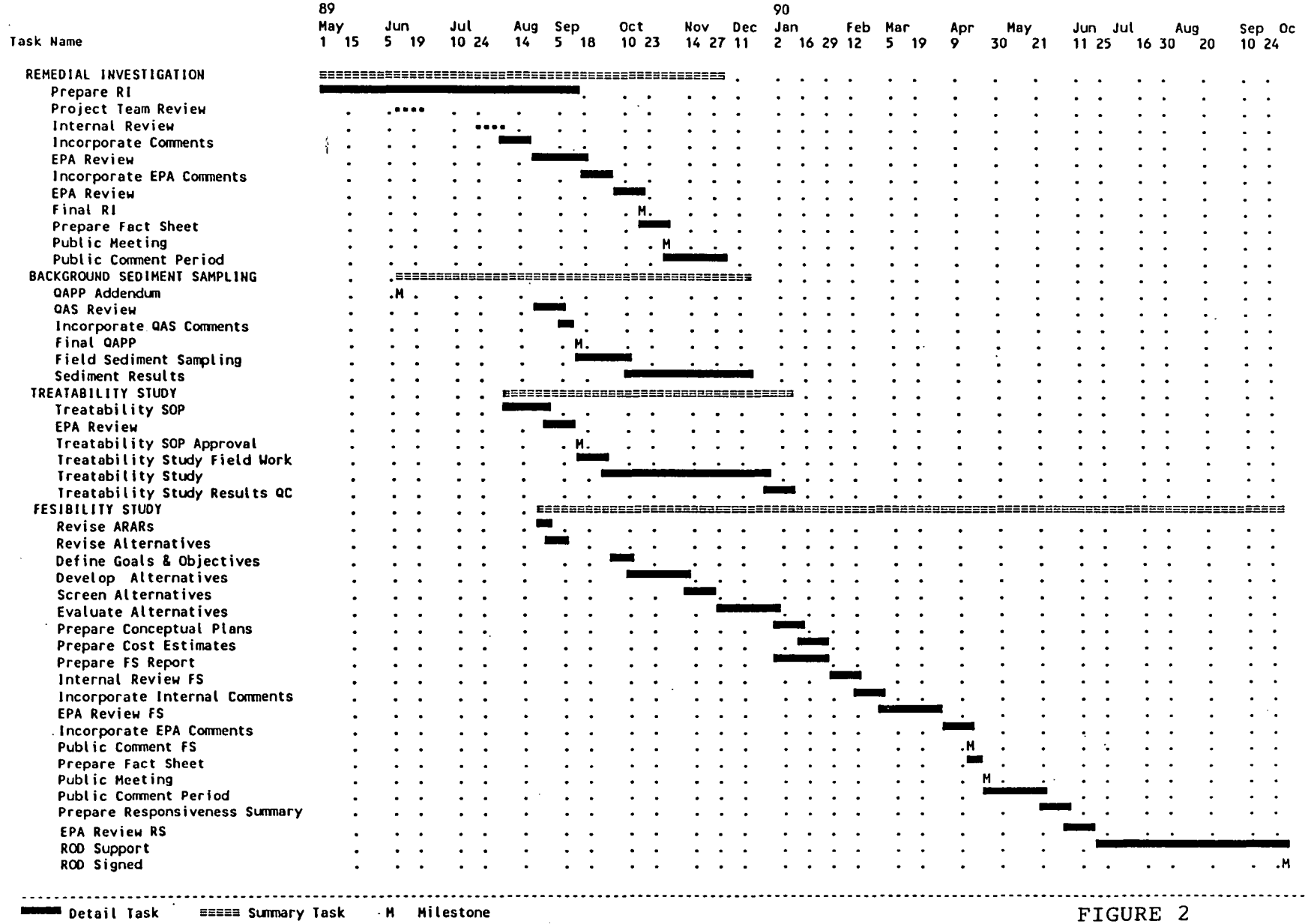

FIGURE 2
PROJECT SCHEDULE
MOSS-AMERICAN QAPP
ADDENDUM 1

Operational responsibilities involving execution and direct management of the technical and administrative aspects of this project have been assigned as follows:

- Regional Project Officer (RPO)
  (U.S. EPA Region V)
- Remedial Project Manager (RPM)
  Betty Lavis (U.S. EPA Region V)
- Site Manager (SM)
  Donald Johnson (CH2M HILL)
- Program Manager (PM)
  John Fleissner (CH2M HILL)

As specified in the Work Plan, the SM accepts primary responsibility for all quality control activities. The SM is, in turn, supervised by the PM. All other positions of responsibility are filled by competent persons as assigned by the SM and PM.

4.2 QUALITY ASSURANCE ORGANIZATION

o Final Review and Approval of QAPP	Betty Lavis, U.S. EPA Region V RPM U.S. EPA Region V QA Officer
o QA review of reports SOPs, and field activities; Auditing of reports, procedures, and activities for identifying and controlling non-conformance for corrective action	Greg Peterson, CH2M HILL, Quality Assurance Manager (QAM)

4.3 FIELD OPERATIONS

o Sample Collections	Don Johnson, CH2M HILL, SM
o Sample Team Leader	Kevin Olson, CH2M HILL
o External Field Audits	U.S. EPA Region V CRL
o Internal Field Audits	Randy Videkovich, CH2M HILL, RTL

4.4 LABORATORIES

Laboratory analysis, data reduction and validation will be performed by the CLP.

- o QA/QC of CLP Data Laboratory Scientific Support Section (LSSS), Central Regional Laboratory (CRL)
- o QA/QC of SAS Data, LSSS, CRL

5.0 SAMPLING PROCEDURES AND SAMPLE CUSTODY

No changes.

6.0 QUALITY ASSURANCE OBJECTIVES

No changes except that samples shall be analyzed according to SOW 7/88 for inorganic analytes and SOW 2/88 for organic analytes.

6.1 FIELD QC AUDITS

No changes.

6.2 ACCURACY, PRECISION, AND SENSITIVITY OF LABORATORY ANALYSIS

No changes.

7.0 ANALYTICAL SERVICES

No changes.

7.1 CLP ROUTINE ANALYTICAL SERVICES

No changes except that samples shall be analyzed according to SOW 7/88 for inorganic analytes and SOW 2/88 for organic analytes. A listing of analytes and CRQLs is provided in Appendix A.

7.2 CLP SPECIAL ANALYTICAL SERVICES

Sediment samples will be analyzed by CLP laboratories using the SAS protocol for low-level PAH and dioxins (see Appendix B).

7.3 CH2M HILL MONTGOMERY LABORATORY SCREENING

No change.

7.4 CLOSE SUPPORT LABORATORY SCREENING

No changes.

7.5 FIELD ANALYTICAL SERVICES

No change.

8.0 QUALITY ASSURANCE REPORTS

No changes.

GLT864/056.50

Appendix A
TARGET COMPOUND LIST

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

Semivolatiles	CAS Number	Quantitation Limits** Water ug/L	Low Soil/Sediment[5] ug/Kg
35. Phenol	108-95-2	10	330
36. bis(2-Chloroethyl) ether	111-44-4	10	330
37. 2-Chlorophenol	95-57-8	10	330
38. 1,3-Dichlorobenzene	541-73-1	10	330
39. 1,4-Dichlorobenzene	106-46-7	10	330
40. Benzyl alcohol	100-51-6	10	330
41. 1,2-Dichlorobenzene	95-50-1	10	330
42. 2-Methylphenol	95-48-7	10	330
43. bis(2-Chloroisopropyl) ether	108-60-1	10	330
44. 4-Methylphenol	106-44-5	10	330
45. N-Nitroso-di-n-dipropylamine	621-64-7	10	330
46. Hexachloroethane	67-72-1	10	330
47. Nitrobenzene	98-95-3	10	330
48. Isophorone	78-59-1	10	330
49. 2-Nitrophenol	88-75-5	10	330
50. 2,4-Dimethylphenol	105-67-9	10	330
51. Benzoic acid	65-85-0	50	1600
52. bis(2-Chloroethoxy) methane	111-91-1	10	330
53 2,4-Dichlorophenol	120-83-2	10	330
54. 1,2,4-Trichlorobenzene	120-82-1	10	330
55. Naphthalene	91-20-3	10	330
56. 4-Chloroaniline	106-47-8	10	330
57. Hexachlorobutadiene	87-68-3	10	330
58. 4-Chloro-3-methylphenol (para-chloro-meta-cresol)	59-50-7	10	330
59. 2-Methylnaphthalene	91-57-6	10	330
60. Hexachlorocyclopentadiene	77-47-4	10	330
61. 2,4,6-Trichlorophenol	88-06-2	10	330
62. 2,4,5-Trichlorophenol	95-95-4	50	1600
63. 2-Chloronaphthalene	91-58-7	10	330
64. 2-Nitroaniline	88-74-4	50	1600
65. Dimethylphthalate	131-11-3	10	330
66. Acenaphthylene	208-96-8	10	330
67. 2,6-Dinitrotoluene	606-20-2	10	330
68. 3-Nitroaniline	99-09-2	50	1600
69. Acenaphthene	83-32-9	10	330

(continued)

Semivolatiles	CAS Number	Quantitation Limits** Water ug/L	Low Soil/Sediment[b] ug/Kg
70. 2,4-Dinitrophenol	51-28-5	50	1600
71. 4-Nitrophenol	100-02-7	50	1600
72. Dibenzofuran	132-64-9	10	330
73. 2,4-Dinitrotoluene	121-14-2	10	330
74. Diethylphthalate	84-66-2	10	330
75. 4-Chlorophenyl-phenyl ether	7005-72-3	10	330
76. Fluorene	86-73-7	10	330
77. 4-Nitroaniline	100-01-6	50	1600
78. 4,6-Dinitro-2-methylphenol	534-52-1	50	1600
79. N-nitrosodiphenylamine	86-30-6	10	330
80. 4-Bromophenyl-phenylether	101-55-3	10	330
81. Hexachlorobenzene	118-74-1	10	330
82. Pentachlorophenol	87-86-5	50	1600
83. Phenanthrene	85-01-8	10	330
84. Anthracene	120-12-7	10	330
85. Di-n-butylphthalate	84-74-2	10	330
86. Fluoranthene	206-44-0	10	330
87. Pyrene	129-00-0	10	330
88. Butylbenzylphthalate	85-68-7	10	330
89. 3,3'-Dichlorobenzidine	91-94-1	20	660
90. Benzo(a)anthracene	56-55-3	10	330
91. Chrysene	218-01-9	10	330
92. bis(2-Ethylhexyl)phthalate	117-81-7	10	330
93. Di-n-octylphthalate	117-84-0	10	330
94. Benzo(b)fluoranthene	205-99-2	10	330
95. Benzo(k)fluoranthene	207-08-9	10	330
96. Benzo(a)pyrene	50-32-8	10	330
97. Indeno(1,2,3-cd)pyrene	193-39-5	10	330
98. Dibenz(a,h)anthracene	53-70-3	10	330
99. Benzo(g,h,i)perylene	191-24-2	10	330

[b] Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for SemiVolatile TCL Compounds are 60 times the individual Low Soil/Sediment CRQL.

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

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

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

Pesticides/PCBs	CAS Number	Quantitation Limits** Water ug/L	Low Soil/Sediment[c] ug/Kg
100. alpha-BHC	319-84-6	0.05	8.0
101. beta-BHC	319-85-7	0.05	8.0
102. delta-BHC	319-86-8	0.05	8.0
103. gamma-BHC (Lindane)	58-89-9	0.05	8.0
104. Heptachlor	76-44-8	0.05	8.0
105. Aldrin	309-00-2	0.05	8.0
106. Heptachlor epoxide	1024-57-3	0.05	8.0
107. Endosulfan I	959-98-8	0.05	8.0
108. Dieldrin	60-57-1	0.10	16.0
109. 4,4'-DDE	72-55-9	0.10	16.0
110. Endrin	72-20-8	0.10	16.0
111. Endosulfan II	33213-65-9	0.10	16.0
112. 4,4'-DDD	72-54-8	0.10	16.0
113. Endosulfan sulfate	1031-07-8	0.10	16.0
114. 4,4'-DDT	50-29-3	0.10	16.0
115. Methoxychlor	72-43-5	0.5	80.0
116. Endrin ketone	53494-70-5	0.10	16.0
117. alpha-Chlordane	5103-71-9	0.5	80.0
118. gamma-Chlordane	5103-74-2	0.5	80.0
119. Toxaphene	8001-35-2	1.0	160.0
120. Aroclor-1016	12674-11-2	0.5	80.0
121. Aroclor-1221	11104-28-2	0.5	80.0
122. Aroclor-1232	11141-16-5	0.5	80.0
123. Aroclor-1242	53469-21-9	0.5	80.0
124. Aroclor-1248	12672-29-6	0.5	80.0
125. Aroclor-1254	11097-69-1	1.0	160.0
126. Aroclor-1260	11096-82-5	1.0	160.0

[c] Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Pesticide/PCB TCL compounds are 15 times the individual Low Soil/Sediment CRQL.

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

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

INORGANIC TARGET ANALYTE LIST (TAL)

Analyte	Contract Required Detection Limit (1,2) (ug/L)
Aluminum	200
Antimony	60
Arsenic	10
Barium	200
Beryllium	5
Cadmium	5
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	3
Magnesium	5000
Manganese	15
Mercury	0.2
Nickel	40
Potassium	5000
Selenium	5
Silver	10
Sodium	5000
Thallium	10
Vanadium	50
Zinc	20
Cyanide	10

(1) Subject to the restrictions specified in the first page of Part G, Section IV of Exhibit D (Alternate Methods - Catastrophic Failure) any analytical method specified in SOW Exhibit D may be utilized as long as the documented instrument or method detection limits meet the Contract Required Detection Limit (CRDL) requirements. Higher detection limits may only be used in the following circumstance:

If the sample concentration exceeds five times the detection limit of the instrument or method in use, the value may be reported even though the instrument or method detection limit may not equal the Contract Required Detection Limit. This is illustrated in the example below:

For lead:

Method in use = ICP
Instrument Detection Limit (IDL) = 40
Sample concentration = 220
Contract Required Detection Limit (CRDL) = 3

The value of 220 may be reported even though instrument detection limit is greater than CRDL. The instrument or method detection limit must be documented as described in Exhibit E.

(2) The CRDL are the instrument detection limits obtained in pure water that must be met using the procedure in Exhibit E. The detection limits for samples may be considerably higher depending on the sample matrix.

Appendix B
SPECIAL ANALYTICAL SERVICES

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

SAS Number
[ ]

SPECIAL ANALYTICAL SERVICES
Regional Request

[x] Regional Transmittal [ ]Telephone Request

A. EPA Region and Site Name:Region V--Moss American

B. Regional Representative: Jan Pels

C. Telephone Number: (312) 353-2720

D. Date of Request:

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

1. General description of analytical service requested:
Analyze sediment samples for low level PAH's.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or Soil and sediments; and whether low, medium, or high concentrations):
Analyze nineteen sediment samples for low level PAH's. Low concentrations are expected.

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

Superfund Remedial

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. Approximate number of days results required after lab receipt of samples:
Laboratory should report results within 35 days after receipt of samples.

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7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
Extraction by Method 3540. Cleanup by Method 3630. Analysis by Method 8100. All methods are modified and copies are attached. All methods are taken from SW-846, Test Methods for Evaluating Solid Waste, Third Edition.

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8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
Required modifications and notes are attached to each method.
Low concentrations are expected.
In the analysis, an attempt shall be made to quantitate all samples before performing any dilutions. If sample dilution is necessary due to excessive background interference the laboratory shall report and provide all raw data and the original chromatogram (before dilution) as well as the chromatograms for all dilutions. If there are any problems with a sample because of this requirement contact the personnel listed in Section III before proceeding with the dilution. Sample results shall be reported on a dry weight basis. Measured percent moisture shall also be reported.
One detection limit verification spike analysis shall be performed. In order to verify the detection limits of the chosen analytical methods a detection limit verification spike sample will be analyzed with each matrix type for this SAS. For sediment and soil samples a 10g. sample of clean washed Ottawa sand shall be spiked in the laboratory to achieve a sample concentration of each analyte at the detection limit requested in the SAS(Section I). The spiked sample will then be extracted, cleaned and analyzed in the same manner as all other samples for this SAS request. The results of these spike samples will be reported with all other analyses.
Matrix spike/matrix spike duplicate analyses shall be performed.

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

The deliverables package shall be as specified in the Organics SOW (2/88). Report all results for blanks, detection limit verification spikes(See Attachment), surrogates, samples, matrix spike and matrix spike duplicates. Include copies of all chromatograms, initial and continuing calibration. All copies must be legible.

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

11. Name of sampling/shipping contact: Dave Shekoski

Phone: (414) 272-2426

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (+/- % or conc.)
Low level PAHs (sediment)	100ug/kg	+/- 20%

(acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, naphthalene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene)

II. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (+/- % or conc.)
Laboratory blanks	at least one per 10 samples and 1 per analytical run.	< Detection limits
Surrogates	Each Sample	40-130% recovery
Matrix spike	1 per 20	40-130% recovery
Matrix spike duplicate	1 per 20	+ or - 20% RPD
Detection Limit Verification Spike	1 per run	Detection limits

III. Action Required if Limits are Exceeded:
Contact Jan Pels, CRL and Joseph A. Sandrin, CH2M Hill.

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

Method 3500 (Organic Extraction and Sample Preparation)
Modification and Notes

Sections not mentioned in the notes are to be applied as written.

Paragraph	Note
2.1	All sample concentrations will be done using a Kuderna-Danish apparatus
2.2	N/A
3.1	N/A
5.2.1	N/A
5.3	Surrogate standards--No deuterated surrogates shall be used.
5.3.1	For PAH analysis using method 8100 the surrogate spiking solution will use 2--fluorobiphenyl 2--fluoronaphthalene
5.3.1.1	Surrogate standard spiking solution shall contain the surrogates at a concentration of 100 ug/ml.
5.4.1	Matrix Spike Standards--The following compounds shall be used for the matrix spiking solution: o Acenaphthene o Pyrene o Benzo(a)anthracene o Benzo(a)pyrene o Benzo(ghi)perylene Standard Spiking Solutions shall contain 100 ug/ml of each constituent.
7.1-7.2	N/A

7.3	Specific cleanup and analysis methods are detailed in the SAS.
8.1	N/A
8.3	Surrogates shall be added to all samples and spikes as specified in the SAS and specific extraction/dilution methods
8.4	Reagent blanks, MS and MSD shall be performed at the frequency specified in the SAS.
8.5.1	N/A
8.5.2	N/A--No QC check sample will be run. The adequacy of the method shall be determined by evaluation of surrogate and MS/MSD results. The analysis of a water matrix QC check sample would use different procedures than those specified for these samples. Analyses of a water matrix QC check sample will not accurately reflect the sediment matrix of these samples.

ORGANIC EXTRACTION AND SAMPLE PREPARATION

1.0 SCOPE AND APPLICATION

1.1 The 3500 Methods are procedures for quantitatively extracting nonvolatile and semivolatile organic compounds from various sample matrices. Cleanup and/or analysis of the resultant extracts are described in Chapter Four, Sections 4.2.2 and 4.3, respectively.

1.2 Method 3580 describes a solvent dilution technique that may be used on non-aqueous nonvolatile and semivolatile organic samples prior to cleanup and/or analysis.

1.3 The 5000 Methods are procedures for preparing samples containing volatile organic compounds for quantitative analysis.

1.4 Refer to the specific method of interest for further details.

2.0 SUMMARY OF METHOD

2.1 3500 Methods: A sample of a known volume or weight is solvent extracted. The resultant extract is dried and then concentrated in a Kuderna-Danish apparatus. Other concentration devices or techniques may be used in place of the Kuderna-Danish concentrator if the quality control requirements of the determinative methods are met (Method 8000, Section 8.0).

2.2 5000 Methods: Refer to the specific method of interest.

3.0 INTERFERENCES

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

3.2 Solvents, reagent, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Chapter One for specific guidance on quality control procedures.

3.3 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

3.4 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.5 Glassware contamination resulting in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorous pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500-mL K-D flask). These items should be hand-rinsed very carefully to avoid this problem.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific method of interest for a description of the apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific method of interest for a description of the solvents needed.

5.2 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions.

5.2.1 Purgeable stock standards: Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood.

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

5.2.1.2 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.

5.2.1.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.1.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.2.1.5 All standards must be replaced after 1 month, or sooner if comparison with check standards indicates a problem.

5.2.2 **Semivolatile stock standards:** Base/neutral and acid stock standards are prepared in methanol. Organochlorine pesticide standards are prepared in acetone.

5.2.2.1 Stock standard solutions should be stored in Teflon-sealed containers at 4°C. 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.

5.3 Surrogate standards: A surrogate standard (i.e., a chemically inert compound not expected to occur in an environmental sample) should be added to each sample, blank, and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits. Recommended surrogates for different analyte groups follow; however, these compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well. Normally three or more standards are added for each analyte group.

5.3.1 **Base/neutral and acid surrogate spiking solutions:** The following are recommended surrogate standards.

Base/neutral	Acid
2-Fluorobiphenyl	2-Fluorophenol
Nitrobenzene-d_5	2,4,6-Tribromophenol
Terphenyl-d_{14}	Phenol-d_6

5.3.1.1 Prepare a surrogate standard spiking solution in methanol that contains the base/neutral compounds at a concentration of 100 ug/mL, and the acid compounds at 200 ug/mL for water and sediment/soil samples (low- and medium-level). For waste samples, the concentration should be 500 ug/mL for base/neutrals and 1000 ug/mL for acids.

5.3.2 **Organochlorine pesticide surrogate spiking solution:** The following are recommended surrogate standards for organochlorine pesticides.

Organochlorine pesticides

Dibutylchlorendate (DBC)
2,4,5,6-Tetrachloro-meta-xylene (TCMX)

5.3.2.1 Prepare a surrogate standard spiking solution at a concentration of 1 ug/mL in acetone for water and sediment/soil samples. For waste samples, the concentration should be 5 ug/mL.

5.3.3 **Purgeable surrogate spiking solution:** The following are recommended surrogate standards for volatile organics.

Purgeable organics
p-Bromofluorobenzene
1,2-Dichloroethane-d_4
Toluene-d_8

5.3.3.1 Prepare a surrogate spiking solution (as described in Paragraph 5.2.1 or through secondary dilution of the stock standard) in methanol containing the surrogate standards at a concentration of 25 ug/mL.

5.4 Matrix spike standards: Select five or more analytes from each analyte group for use in a spiking solution. The following are recommended matrix spike standard mixtures for a few analyte groups. These compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well.

5.4.1 **Base/neutral and acid matrix spiking solution:** Prepare a spiking solution in methanol that contains each of the following base/neutral compounds at 100 ug/mL and the acid compounds at 200 ug/mL for water and sediment/soil samples. The concentration of these compounds should be five times higher for waste samples.

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

5.4.2 **Organochlorine pesticide matrix spiking solution:** Prepare a spiking solution in acetone or methanol that contains the following pesticides in the concentrations specified for water and sediment/soil. The concentration should be five times higher for waste samples.

Pesticide	Concentration (ug/mL)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4'-DDT	0.5

5.4.3 **Purgeable matrix spiking solution:** Prepare a spiking solution in methanol that contains the following compounds at a concentration of 25 ug/mL.

Purgeable organics

1,1-Dichloroethene
Trichloroethene
Chlorobenzene
Toluene
Benzene

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to the Organic Analyte Chapter, Section 4.1.

7.0 PROCEDURE

7.1 Semivolatile organic sample extraction: Water, soil/sediment, sludge, and waste samples requiring analysis for base/neutral and acid extractables and/or organochlorine pesticides must undergo solvent extraction prior to analysis. This manual contains four methods that may be used for this purpose: Method 3510; Method 3520; Method 3540; and Method 3550. The method that should be used on a particular sample, is highly dependent upon the physical characteristics of that sample. Therefore, review these four methods prior to choosing one in particular. Appropriate surrogate standards and, if necessary, matrix spiking solutions are added to the sample prior to extraction for all four methods.

7.1.1 **Method 3510:** Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is solvent extracted using a separatory funnel. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Method 3520 should be used if an emulsion forms between the solvent-sample phases, which can not be broken up by mechanical techniques.

7.1.2 **Method 3520:** Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is extracted with an organic solvent in a continuous liquid-liquid extractor. The solvent must have a density greater than that of the sample. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. The limitations of Method 3510 concerning solvent-sample phase separation do not interfere with this procedure.

7.1.3 **Method 3540:** This is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.4 **Method 3550:** This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using the technique of sonication. Two procedures are detailed depending upon the expected concentration of organics in the sample; a low concentration and a high concentration method. In both, a known weight of sample is mixed with anhydrous sodium sulfate and solvent extracted using sonication. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.5 **Method 3580:** This method describes the technique of solvent dilution of non-aqueous waste samples. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are soluble in the dilution solvent.

7.2 Volatile organic sample preparation: There are three methods for volatile sample preparation: Method 5030; Method 5040; and direct injection. Method 5030 is the most widely applicable procedure for analysis of volatile organics, while the direct injection technique may have limited applicability to aqueous matrices.

7.2.1 **Method 5030:** This method describes the technique of purge-and-trap for the introduction of purgeable organics into a gas chromatograph. This procedure is applicable for use with aqueous samples directly and to solids, wastes, soils/sediments, and water-miscible liquids following appropriate preparation. An inert gas is bubbled through the sample, which will efficiently transfer the purgeable organics from the aqueous phase to the vapor phase. The vapor phase is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. Prior to application of the purge-and-trap procedure, all samples (including blanks, spikes, and duplicates) should be spiked with surrogate standards and, if required, with matrix spiking compounds.

7.2.2 **Method 5040:** This method is applicable to the investigation of sorbent cartridges from volatile organic sampling train (VOST).

7.3 Sample analysis: Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. For samples requiring volatile organic analysis, application of one of the three methods described above is followed directly by gas chromatographic analysis (Methods 8010, 8015, 8020, or 8030). Samples prepared for semivolatile analysis may, if necessary, undergo cleanup (See Method 3600) prior to application of a specific determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific guidance on quality control procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water blank that all glassware and reagents are interference free. Each time a set of samples are processed, a method blank(s) should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Surrogate standards should be added to all samples when specified in the appropriate determinative method in Chapter Four, Section 4.3.

8.4 A reagent blank, a matrix spike, and a duplicate or matrix spike duplicate must be performed for each analytical batch (up to a maximum of 20 samples) analyzed.

8.5 For GC or GC/MS analysis, the analytical system performance must be verified by analyzing quality control (QC) check samples. Method 8000, Section 8.0 discusses in detail the process of verification; however, preparation of the QC check sample concentrate is dependent upon the method being evaluated.

8.5.1 **Volatile organic QC check samples:** QC check sample concentrates containing each analyte of interest are spiked into reagent water (defined as the QC check sample) and analyzed by purge-and-trap (Method 5030). The concentration of each analyte in the QC check sample is 20 ug/L. The evaluation of system performance is discussed in detail in Method 8000, beginning with Paragraph 8.6.

8.5.2 **Semivolatile organic QC check samples:** To evaluate the performance of the analytical method, the QC check samples must be handled in exactly the same manner as actual samples. Therefore, 1.0 mL of the QC check sample concentrate is spiked into each of four 1-L aliquots of reagent water (now called the QC check sample), extracted, and then analyzed by GC. The variety of semivolatile analytes which may be analyzed by GC is such that the concentration of the QC check sample concentrate is different for the different analytical techniques presented in the manual. Method 8000 discusses in detail the procedure of verifying the detection system once the QC check sample has been prepared. The concentrations of the QC check sample concentrate for the various methods are as follows:

8.5.2.1 Method 8040 - Phenols: The QC check sample concentrate should contain each analyte at a concentration of 100 ug/mL in 2-propanol.

8.5.2.2 Method 8060 - Phthalate esters: The QC check sample concentrate should contain the following analytes at the following concentrations in acetone: butyl benzyl phthalate, 10 ug/mL; bis(2-ethylhexyl)phthalate, 50 ug/mL; di-n-octylphthalate, 50 ug/mL; and any other phthalate at 25 ug/mL.

8.5.2.3 Method 8080 - Organochlorine pesticides and PCBs: The QC check sample concentrate should contain each single-component analyte at the following concentrations in acetone: 4,4'-DDD, 10 ug/mL; 4,4'-DDT, 10 ug/mL; endosulfan II, 10 ug/mL; endosulfan sulfate, 10 ug/mL; and any other single-component pesticide at 2 ug/mL. If the method is only to be used to analyze PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 ug/mL in acetone.

8.5.2.4 Method 8090 - Nitroaromatics and Cyclic Ketones: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: each dinitrotoluene at 20 ug/mL; and isophorone and nitrobenzene at 100 ug/mL.

8.5.2.5 Method 8100 - Polynuclear aromatic hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene 5 ug/mL; and any other PAH at 10 ug/mL.

8.5.2.6 Method 8120 - Chlorinated hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: hexachloro-substituted hydrocarbons, 10 ug/mL; and any other chlorinated hydrocarbon, 100 ug/mL.

9.0 METHOD PERFORMANCE

9.1 The recovery of surrogate standards is used to monitor unusual matrix effects, sample processing problems, etc. The recovery of matrix spiking compounds indicates the presence or absence of unusual matrix effects.

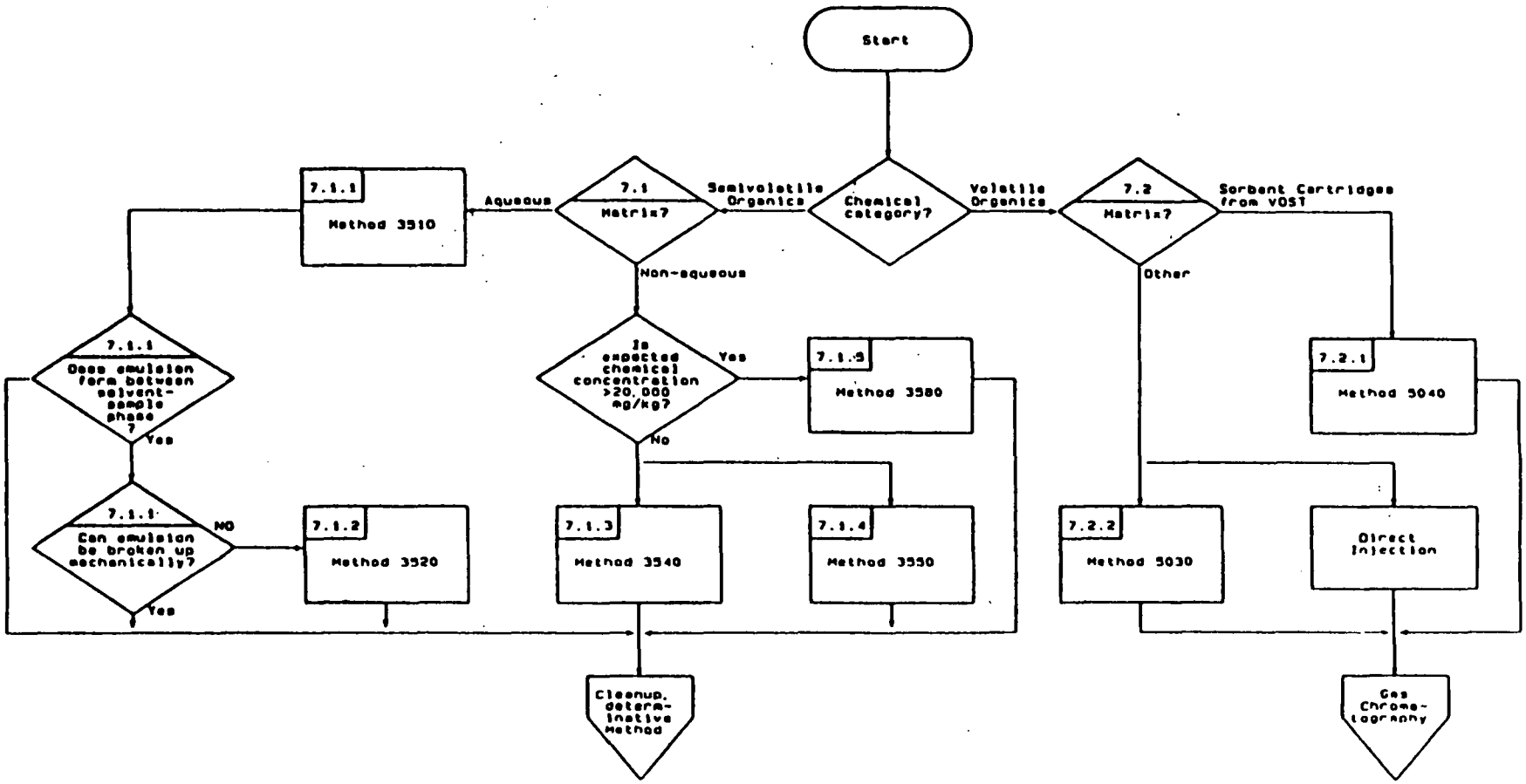
9.2 The performance of this method will be dictated by the overall performance of the sample preparation in combination with the analytical determinative method.

10.0 REFERENCES

10.1 None required.

METHOD 3500

ORGANIC EXTRACTION AND SAMPLE PREPARATION



Method 3540 (Soxhlet Extraction)

Sections not mentioned in notes are to be applied as written.

Paragraph	Note
2.0	In all cases an extraction thimble shall be used to hold the sample.
4.11	Soil and solids samples should be ground before extraction.
5.3	Use toluene/methanol (5.3.1.1) for extraction of all samples.
7.1.1	Use this procedure for all samples.
7.1.2	N/A
7.2	Sample results are required on a dry weight basis. Percent moisture will be determined.
7.2.1	Use 5 g of sample.
7.3	Refer to method 3500 for PAH surrogates.
7.9	For PAH analysis the exchange solvent is cyclohexane.
7.12	Proceed to Cleanup method 3630 for PAHs.

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor: 40-mm I.D., with 500-mL round-bottom flask.

4.2 Drying column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Vials: Glass, 2-mL capacity, with Teflon-lined screw cap.

4.7 Glass or paper thimble or glass wool: Contaminant free.

4.8 Heating mantle: Rheostat controlled.

4.9 Syringe: 5-mL.

4.10 Apparatus for determining percent moisture:

4.10.1 Oven: Drying.

4.10.2 Desiccator.

4.10.3 Crucibles: Porcelain.

4.11 Apparatus for grinding: If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue Number 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples, except gummy, fibrous, or oily materials.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Sodium sulfate: (ACS) Granular anhydrous (purified by washing with methylene chloride followed by heating at 400°C for 4 hr in a shallow tray).

5.3 Extraction solvents:

5.3.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems.

5.3.1.1 Toluene/Methanol: 10:1 (v/v), pesticide quality or equivalent.

5.3.1.2 Acetone/Hexane: 1:1 (v/v), pesticide quality or equivalent.

5.3.2 Other samples shall be extracted using the following:

5.3.2.1 Methylene chloride: pesticide quality or equivalent.

5.4 Exchange solvents: Hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample handling:

7.1.1 **Sediment/soil samples:** Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 **Waste samples:** Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 **Dry waste samples amenable to grinding:** Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of percent moisture: In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

7.3 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (See Method 3500 for details on the surrogate standard and matrix spiking solutions.) For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.4 Place 300 mL of the extraction solvent (Section 5.3) into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hr.

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

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

7.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100-125 mL of extraction solvent to complete the quantitative transfer.

7.8 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Paragraph 7.6, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Paragraph 7.9 or adjusted to 10.0 mL with the solvent last used.

TABLE 1. SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8120	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	-	-	1.0
8270[a,c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0

[a] To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b] Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

7.11 If further concentration is indicated in Table 1, add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.12 The extracts obtained may now be analyzed for analyte content using a variety of organic techniques (see Section 4.3 of this chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a Teflon-sealed screw-cap vial and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

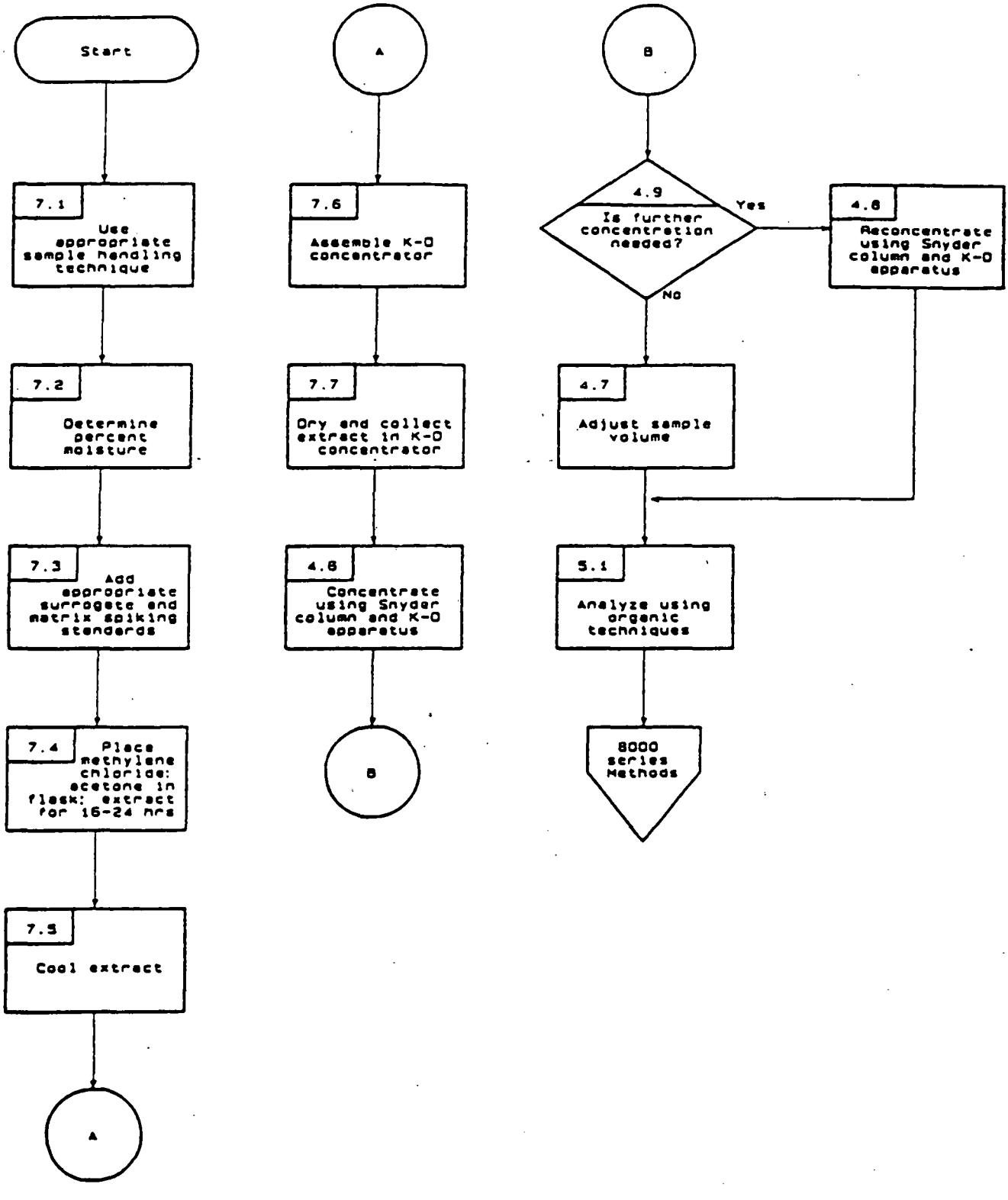
8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.


Start
7.1 Use appropriate sample handling technique
7.2 Determine percent moisture
7.3 Add appropriate surrogate and matrix spiking standards
7.4 Place methylene chloride: acetone in flask; extract for 16-24 hrs
7.5 Cool extract
A
A
7.6 Assemble K-D concentrator
7.7 Dry and collect extract in K-D concentrator
4.8 Concentrate using Snyder column and K-D apparatus
B
B
4.9 Is further concentration needed?
Yes
No
4.8 Reconcentrate using Snyder column and K-D apparatus
4.7 Adjust sample volume
5.1 Analyze using organic techniques
8000 series Methods

CLEANUP

1.0 SCOPE AND APPLICATION

1.1 General:

1.1.1 Injection of extracts into a gas or liquid chromatograph can cause extraneous peaks, deterioration of peak resolution and column efficiency, and loss of detector sensitivity and can greatly shorten the lifetime of expensive columns. The following techniques have been applied to extract purification: partitioning between immiscible solvents; adsorption chromatography; gel permeation chromatography; chemical destruction of interfering substances with acid, alkali, or oxidizing agents; and distillation. These techniques may be used individually or in various combinations, depending on the extent and nature of the co-extractives.

1.1.2 It is an unusual situation, e.g., with some water samples, when extracts can be directly determined without further treatment. Soil and waste extracts often require a combination of cleanup methods. For example, when analyzing for organochlorine pesticides and PCBs, it may be necessary to use gel permeation chromatography (GPC), to eliminate the high boiling material and a micro alumina or Florisil column to eliminate interferences with the analyte peaks on the GC/ECD.

1.2 Specific:

1.2.1 **Adsorption column chromatography:** Alumina (Methods 3610 and 3611), Florisil (Method 3620), and silica gel (Method 3630) are useful for separating analytes of a relatively narrow polarity range away from extraneous, interfering peaks of a different polarity.

1.2.2 **Acid-base partitioning:** Useful for separating acidic or basic organics from neutral organics. It has been applied to analytes such as the chlorophenoxy herbicides and phenols.

1.2.3 **Gel permeation chromatography** (GPC): The most universal cleanup technique for a broad range of semivolatile organics and pesticides. It is capable of separating high molecular-weight material from the sample analytes. It has been used successfully for all the semivolatile base, neutral, and acid compounds associated with the EPA Priority Pollutant and the Superfund Hazardous Substance Lists. GPC is usually not applicable for eliminating extraneous peaks on a chromatogram which interfere with the analytes of interest.

1.2.4 **Sulfur cleanup:** Useful in eliminating sulfur from sample extracts, which may cause chromatographic interference with analytes of interest.

1.2.5 Table 1 indicates the recommended cleanup techniques for the indicated groups of compounds. This information can also be used as guidance for compounds that are not listed. Compounds that are chemically similar to these groups of compounds should follow a similar elution pattern.

2.0 SUMMARY OF METHOD

2.1 Refer to the specific cleanup method for a summary of the procedure.

3.0 INTERFERENCES

3.1 Analytical interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free of interferences, under the conditions of the analysis, by running laboratory reagent blanks.

3.2 More extensive procedures than those outlined in the methods may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific cleanup method for apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific cleanup method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Prior to using the cleanup procedures, samples should undergo solvent extraction. Chapter Two, Section 2.3.3, may be used as a guide for choosing the appropriate extraction procedure based on the physical composition of the waste and on the analytes of interest in the matrix (see also Method 3500 for a general description of the extraction technique). For some organic liquids, extraction prior to cleanup may not be necessary

7.2 In most cases, the extracted sample is then analyzed by one of the determinative methods available in Section 4.3 of this chapter. If the analytes of interest are not able to be determined due to interferences, cleanup is performed.

TABLE 1. RECOMMENDED CLEANUP TECHNIQUES FOR INDICATED GROUPS OF COMPOUNDS

Analyte Group	Determinative[a] Method	Cleanup Method Option
Phenols	8040	3630[b], 3640, 3650, 8040[c]
Phthalate esters	8060	3610, 3620, 3640
Nitrosamines	8070	3610, 3620, 3640
Organochlorine pesticides & PCBs	8080	3620, 3640, 3660
Nitroaromatics and cyclic ketones	8090	3620, 3640
Polynuclear aromatic hydrocarbons	8100	3611, 3630, 3640
Chlorinated hydrocarbons	8120	3620, 3640
Organophosphorous pesticides	8140	3620, 3640
Chlorinated herbicides	8150	8150[d]
Priority pollutant semivolatiles	8250, 8270	3640, 3650, 3660
Petroleum waste	8250, 8270	3611, 3650

[a] The GC/MS Methods, 8250 and 8270, are also appropriate determinative methods for all analyte groups, unless lower detection limits are required.

[b] Cleanup applicable to derivatized phenols.

[c] Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.

[d] Method 8150 incorporates an acid-base cleanup step as an integral part of the method.

7.3 Many of the determinative methods specify cleanup methods that should be used when determining particular analytes; e.g., Method 8060 (gas chromatography of phthalate esters) recommends using either Method 3610 (Alumina column cleanup) or Method 3620 (Florisil column cleanup) if interferences prevent analysis. However, the experience of the analyst may prove invaluable in determining which cleanup methods are needed. As indicated in Section 1.0 of this method, many matrices may require a combination of cleanup procedures in order to ensure proper analytical determinations.

7.4 Guidance for cleanup is specified in each of the methods that follow. The amount of extract cleanup required prior to the final determination depends on the selectivity of both the extraction procedure and the determinative method and the required detection limit.

7.5 Following cleanup, the sample is concentrated to whatever volume is required in the determinative method. Analysis follows as specified in the determinative procedure (Section 4.3 of this chapter).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered by the cleanup technique before the cleanup is applied to actual samples.

8.2 For sample extracts that are cleaned up, the associated quality control samples (e.g., spikes, blanks, and duplicates) must also be processed through the same cleanup procedure.

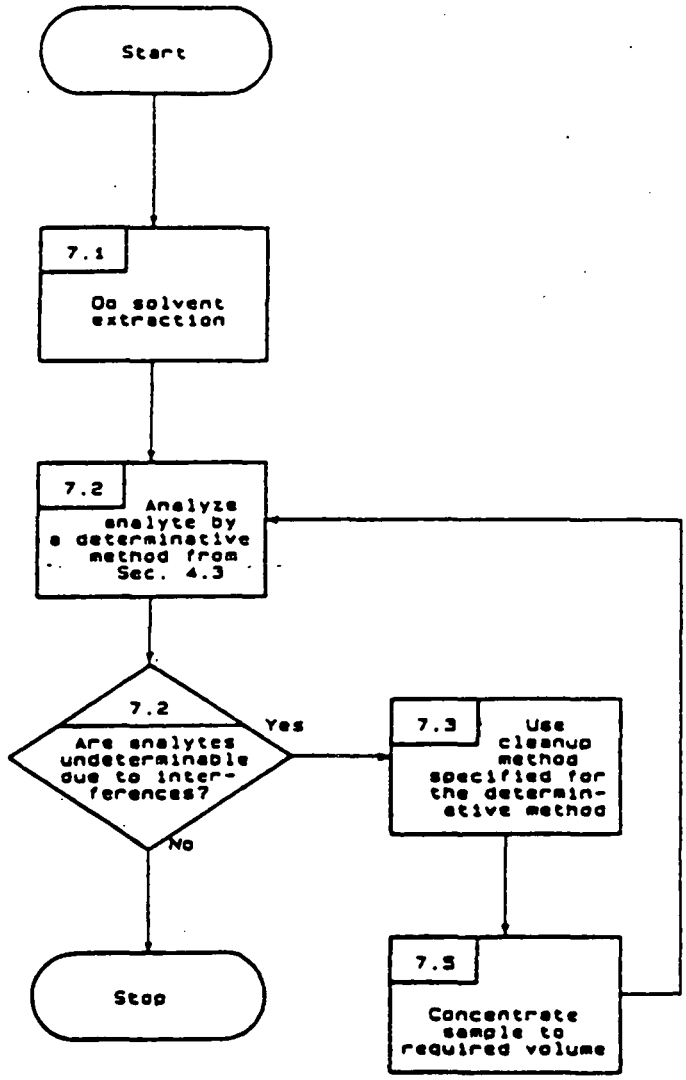
8.3 The analysis using each determinative method (GC, GC/MS, HPLC) specifies instrument calibration procedures using stock standards. It is recommended that cleanup also be performed on a series of the same type of standards to validate chromatographic elution patterns for the compounds of interest and to verify the absence of interferences from reagents.

9.0 METHOD PERFORMANCE

9.1 Refer to the specific cleanup method for performance data.

10.0 REFERENCES

10.1 Refer to the specific cleanup method.


Start
7.1
Do solvent extraction
7.2
Analyze analyte by a determinative method from Sec. 4.3
7.2
Are analytes undeterminable due to interferences?
Yes
No
7.3
Use cleanup method specified for the determinative method
7.5
Concentrate sample to required volume
Stop

Method 3630 (Silica Gel Cleanup)

Sections not mentioned in the notes are to be applied as written

Paragraph	Notes
7.1	Use the entire solvent concentrate for the cleanup procedure

SILICA GEL CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is for separating the analytes from interfering compounds of a different chemical polarity.

1.2 General applications (Gordon and Ford):

1.2.1 **Activated:** Heated at 150-160°C for several hours. USES: Separation of hydrocarbons.

1.2.2 **Deactivated:** Containing 10-20% water. USES: An adsorbent for most functionalities with ionic or nonionic characteristics, including alkaloids, sugar esters, glycosides, dyes, alkali metal cations, lipids, glycerides, steroids, terpenoids and plasticizers. The disadvantages of deactivated silica gel are that the solvents methanol and ethanol decrease adsorbent activity.

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing polynuclear aromatic hydrocarbons and derivatized phenolic compounds.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Chromatographic column: 250-mm long x 10-mm I.D.; with Pyrex glass wool at bottom and a Teflon stopcock.
NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits

may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers: 500-mL.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask: 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

4.3.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Muffle furnace.

4.5 Reagent bottle: 500-mL.

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.8 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

5.1 Silica gel: 100/200 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr at 130°C in a shallow glass tray, loosely covered with foil.

5.2 Sodium sulfate (ACS): Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.3 Eluting solvents: Cyclohexane, hexane, 2-propanol, toluene, methylene chloride, pentane (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Polynuclear aromatic hydrocarbons:

7.1.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. Add 1 to 10 mL of the sample extract (in methylene chloride) and a boiling chip to a clean K-D concentrator tube. Add 4 mL of cyclohexane and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride to the top. Place the micro-K-D apparatus on a boiling (100°C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of cyclohexane. Adjust the extract volume to about 2 mL.

7.1.2 Prepare a slurry of 10 g of activated silica gel in methylene chloride and place this into a 10-mm I.D. chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

7.1.3 Preelute the column with 40 mL of pentane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane eluate.

7.1.4 Next, elute the column with 25 mL of methylene chloride/-pentane (2:3)(v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction to whatever volume is required (1-10 mL). Proceed with HPLC or GC analysis. Components that elute in this fraction are:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(ghi)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene

Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

7.2 Derivatized phenols:

7.2.1 This silica gel cleanup procedure is performed on sample extracts that have undergone pentafluorobenzyl bromide derivatization as described in Method 8040.

7.2.2 Place 4.0 g of activated silica gel into a 10-mm I.D. chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top of the silica gel.

7.2.3 Preelute the column with 6 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, pipet onto the column 2 mL of the hexane solution that contains the derivatized sample or standard. Elute the column with 10.0 mL of hexane and discard the eluate.

7.2.4 Elute the column, in order, with: 10.0 mL of 15% toluene in hexane (Fraction 1); 10.0 mL of 40% toluene in hexane (Fraction 2); 10.0 mL of 75% toluene in hexane (Fraction 3); and 10.0 mL of 15% 2-propanol in toluene (Fraction 4). All elution mixtures are prepared on a volume:volume basis. Elution patterns for the phenolic derivatives are shown in Table 1. Fractions may be combined, as desired, depending upon the specific phenols of interest or level of interferences. Proceed with GC analysis (Method 8040).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides performance information on the fractionation of phenolic derivatives using this method.

10.0 REFERENCES

1. Gordon, A.J., and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References, (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1. SILICA GEL FRACTIONATION OF PFBB DERIVATIVES

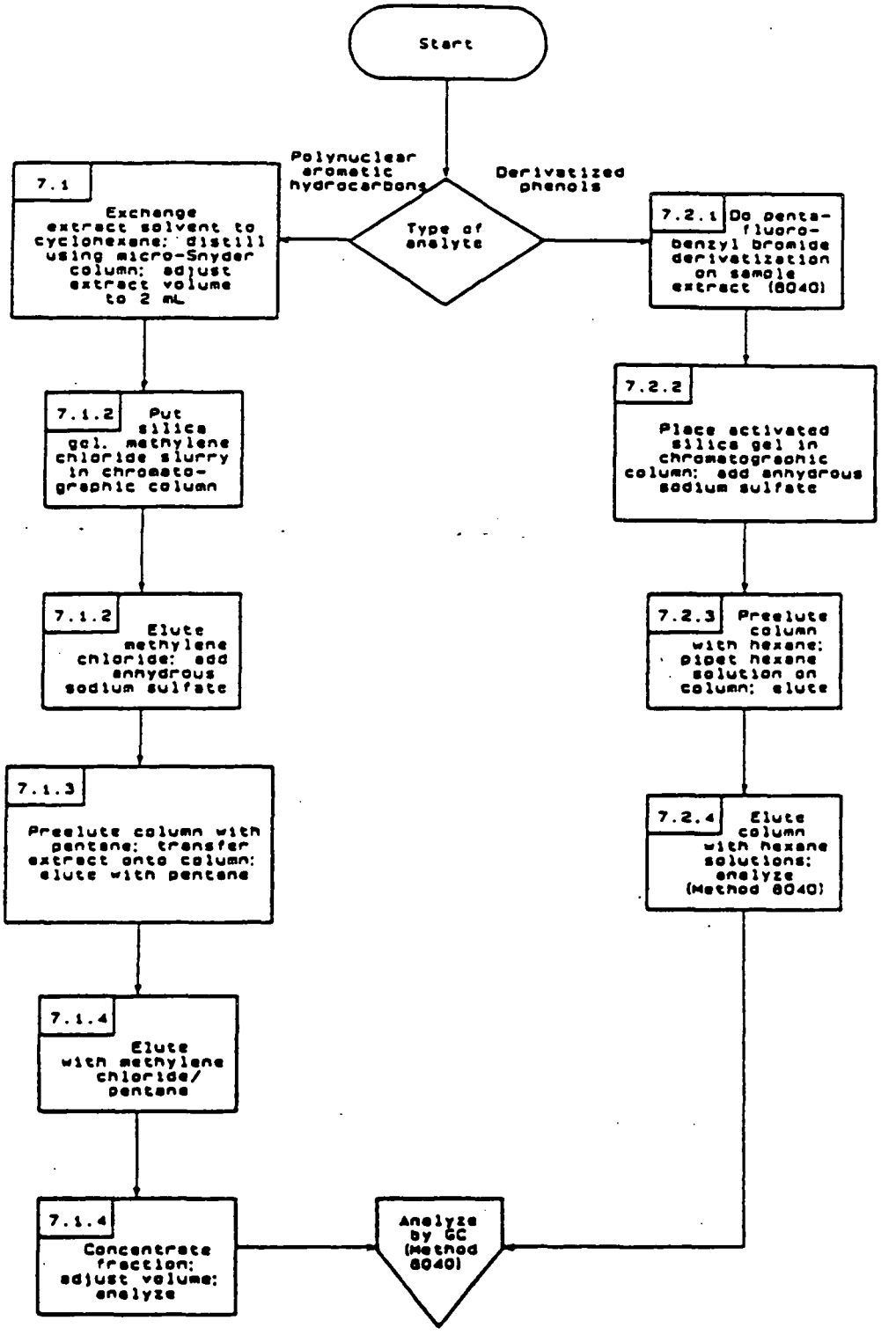
Parameter	Percent Recovery by Fraction[1]			
	1	2	3	4
2-Chlorophenol		90	1	
2-Nitrophenol			9	90
Phenol		90	10	
2,4-Dimethylphenol		95	7	
2,4-Dichlorophenol		95	1	
2,4,6-Trichlorophenol	50	50		
4-Chloro-3-methylphenol		84	14	
Pentachlorophenol	75	20		
4-Nitrophenol			1	90

[1] Eluant composition:

Fraction 1-15% toluene in hexane.
Fraction 2-40% toluene in hexane.
Fraction 3-75% toluene in hexane.
Fraction 4-15% 2-propanol in toluene.

METHOD 3630

SILICA GEL CLEANUP



Method 8000 (Gas Chromatography)

Sections not mentioned in the notes are to be applied as written.

Paragraph	Note
7.4	External calibration shall be used for all samples.
7.6.9.1	Confirmation shall be accomplished on a second GC column.
8.3	Reagent blanks, MS and MSD analyses shall be run at the frequency specified in the SAS.
8.6	No QC check sample will be run for reasons listed in modifications to Method 3500.

METHOD 8000

GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Gas chromatography is a quantitative analytical technique useful for organic compounds capable of being volatilized without being decomposed or chemically rearranged. Gas chromatography (GC), also known as vapor phase chromatography (VPC), has two subcategories distinguished by: gas-solid chromatography (GSC), and gas-liquid chromatography (GLC) or gas-liquid partition chromatography (GLPC). This last group is the most commonly used, distinguished by type of column adsorbent or packing.

1.2 The gas chromatographic methods are recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 SUMMARY OF METHOD

2.1 Each organic analytical method that follows provides a recommended technique for extraction, cleanup, and occasionally, derivatization of the samples to be analyzed. Before the prepared sample is introduced into the GC, a procedure for standardization must be followed to determine the recovery and the limits of detection for the analytes of interest. Following sample introduction into the GC, analysis proceeds with a comparison of sample values with standard values. Quantitative analysis is achieved through integration of peak area or measurement of peak height.

3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with reagent water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or of reagent water to check for cross contamination. For volatile samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak areas is recommended.

4.2 Gas chromatographic columns: See the specific determinative method. Other packed or capillary (open-tubular) columns may be used if the requirements of Section 8.6 are met.

5.0 REAGENTS

5.1 See the specific determinative method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Extraction: Adhere to those procedures specified in the referring determinative method.

7.2 Cleanup and separation: Adhere to those procedures specified in the referring determinative method.

7.3 The recommended gas chromatographic columns and operating conditions for the instrument are specified in the referring determinative method.

7.4 Calibration:

7.4.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.0 of the determinative method of interest. Prepare calibration standards using the procedures indicated in Section 5.0 of the determinative method of interest. Calibrate the chromatographic system using either the external standard technique (Section 7.4.2) or the internal standard technique (Section 7.4.3).

7.4.2 External standard calibration procedure:

7.4.2.1 For each analyte of interest, prepare calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.2.2 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g, 2- to 5-uL injections, purge-and-trap, etc.). Tabulate peak height or area responses against the mass injected.

The results can be used to prepare a calibration curve for each analyte. Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

$$\text{Calibration factor} = \frac{\text{Total Area of Peak}^*}{\text{Mass injected (in nanograms)}}$$

*For multiresponse pesticides/PCBs use the total area of all peaks used for quantitation.

7.4.2.3 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than ±15%, a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100$$

where:

R_1 = Calibration Factor from first analysis.

R_2 = Calibration Factor from succeeding analyses.

7.4.3 **Internal standard calibration procedure:**

7.4.3.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.4.3.2 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with an appropriate solvent.

One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.3.3 Inject each calibration standard using the same introduction technique that will be applied to the actual samples (e.g, 2- to 5-uL injection, purge-and-trap, etc.). Tabulate the peak height or area responses against the concentration of each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the analyte to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard, ug/L.

C_s = Concentration of the analyte to be measured, ug/L.

If the RF value over the working range is constant (<20% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} versus RF.

7.4.3.4 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than ±15%, a new calibration curve must be prepared for that compound.

7.5 Retention time windows:

7.5.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all single component standard mixtures and multiresponse products (i.e., PCBs) throughout the course of a 72-hr period. Serial injections over less than a 72-hr period result in retention time windows that are too tight.

7.5.2 Calculate the standard deviation of the three absolute retention times for each single component standard. For multiresponse products, choose one major peak from the envelope and calculate the

standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples.

7.5.2.1 Plus or minus three times the standard deviation of the absolute retention times for each standard 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 products (i.e., PCBs), the analyst should use the retention time window but should primarily rely on pattern recognition.

7.5.2.2 In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

7.5.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

7.6 Gas chromatographic analysis:

7.6.1 Introduction of organic compounds into the gas chromatograph varies depending on the volatility of the compound. Volatile organics are primarily introduced by purge-and-trap (Method 5030). However, there are limited applications where direct injection is acceptable. Use of Method 3810 or 3820 as a screening technique for volatile organic analysis may be valuable with some sample matrices to prevent overloading and contamination of the GC systems. Semivolatile organics are introduced by direct injection.

7.6.2 The appropriate detector(s) is given in the specific method.

7.6.3 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with multilevel calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.6.4 **Direct Injection:** Inject 2-5 uL of the sample extract using the solvent flush technique. Smaller (1.0-uL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 uL and the resulting peak size in area units or peak height.

7.6.5 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.6.6 If peak detection is prevented by the presence of interferences, further cleanup is required.

7.6.7 Examples of chromatograms for the compounds of interest are frequently available in the referring analytical method.

7.6.8 Calibrate the system immediately prior to conducting any analyses (see Paragraph 7.4). A midlevel standard must also be injected at intervals specified in the method and at the end of the analysis sequence. The calibration factor for each analyte to be quantitated, must not exceed a 15% difference when compared to the initial standard of the analysis sequence. When this criteria is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary (see Section 7.7) before recalibrating and proceeding with sample analysis. All samples that were injected after the sample exceeding the criteria must be reinjected.

7.6.9 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte from Section 7.6.8 as the midpoint of the window for that day. The daily retention time window equals the midpoint $\pm$ three times the standard deviation determined in Section 7.5.

7.6.9.1 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Normally, confirmation is required: on a second GC column; by GC/MS if concentration permits; or by other recognized confirmation techniques. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.

7.6.9.2 Validation of GC system qualitative performance: Use the midlevel standards interspersed throughout the analysis sequence (Paragraph 7.6.8) to evaluate this criterion. If any of the standards fall outside their daily retention time window, the system is out of control. Determine the cause of the problem and correct it (see Section 7.7).

7.7 Suggested chromatography system maintenance: Corrective measures may require any one or more of the following remedial actions.

7.7.1 **Packed columns:** For instruments with injection port traps, 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 the packing material if any discoloration is noted, also swab out the inside walls of the column if any residue is noted. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described in Section 7.7.3) and/or repack/replace the column.

7.7.2 **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.

7.7.3 **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 noticeable foreign material.

7.7.3.1 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.

7.7.3.2 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.

7.8 Calculations:

7.8.1 **External standard calibration:** The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the calibration curve or the calibration factor determined in Paragraph 7.4.2. The concentration of a specific analyte is calculated as follows:

Aqueous samples:

$$\text{Concentration (ug/L)} = [(A_x)(A)(V_t)(D)]/[(A_s)(V_i)(V_s)]$$

where:

A_x = Response for the analyte in the sample, units may be in area counts or peak height.

A = Amount of standard injected or purged, ng.

A_s = Response for the external standard, units same as for A_x.

V_i = Volume of extract injected, uL. For purge-and-trap analysis, V_i is not applicable and therefore = 1.

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

V_t = Volume of total extract, uL. For purge-and-trap analysis, V_t is not applicable and therefore = 1.

V_s = Volume of sample extracted or purged, mL.

Nonaqueous samples:

$$\text{Concentration (ng/g)} = [(A_x)(A)(V_t)(D)]/[(A_s)(V_i)(W)]$$

where:

W = Weight of sample extracted or purged, g. The wet weight or dry weight may be used, depending upon the specific applications of the data.

A_x, A_s, A, V_t, D, and V_i have the same definition as for aqueous samples.

7.8.2 Internal standard calibration: For each analyte of interest, the concentration of that analyte in the sample is calculated as follows:

Aqueous samples:

$$\text{Concentration (ug/L)} = [(A_x)(C_{is})(D)]/[(A_{is})(RF)(V_s)]$$

where:

A_x = Response of the analyte being measured, units may be in area counts or peak height.

C_{is} = Amount of internal standard added to extract or volume purged, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = Response of the internal standard, units same as A_x.

RF = Response factor for analyte, as determined in Paragraph 7.4.3.3.

V_s = Volume of water extracted or purged, mL.

Nonaqueous samples:

$$\text{Concentration (ug/kg)} = [(A_s)(C_{is})(D)]/[(A_{is})(RF)(W_s)]$$

where:

W_s = Weight of sample extracted, g. Either a dry weight or wet weight may be used, depending upon the specific application of the data.

A_s, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike and matrix spike duplicate/duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

8.4 The experience of the analyst performing gas chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g, column changed), recalibration of the system must take place.

8.5 Required instrument QC:

8.5.1 Section 7.4 requires that the %RSD vary by <20% when comparing calibration factors to determine if a five point calibration curve is linear.

8.5.2 Section 7.4 sets a limit of ±15% difference when comparing daily response of a given analyte versus the initial response. If the limit is exceeded, a new standard curve must be prepared.

8.5.3 Section 7.5 requires the establishment of retention time windows.

8.5.4 Paragraph 7.6.8 sets a limit of ±15% difference when comparing the initial response of a given analyte versus any succeeding standards analyzed during an analysis sequence.

8.5.5 Paragraph 7.6.9.2 requires that all succeeding standards in an analysis sequence must fall within the daily retention time window established by the first standard of the sequence.

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

8.6.1 A quality (QC) check sample concentrate is required containing each analyte of interest. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.6.1.1 The concentration of the QC check sample concentrate is highly dependent upon the analytes being investigated. Therefore, refer to Method 3500, Section 8.0 for the required concentration of the QC check sample concentrate.

8.6.2 Preparation of QC check samples:

8.6.2.1 Volatile organic analytes (Methods 8010, 8020, and 8030): The QC check sample is prepared by adding 200 uL of the QC check sample concentrate (Section 8.6.1) to 100 mL of reagent water.

8.6.2.2 Semivolatile organic analytes (Methods 8040, 8060, 8080, 8090, 8100, and 8120): The QC check sample is prepared by adding 1.0 mL of the QC check sample concentrate (8.6.1) to each of four 1-L aliquots of reagent water.

8.6.3 Four aliquots of the well-mixed QC check sample are analyzed by the same procedures used to analyze actual samples (Section 7.0 of each of the methods). For volatile organics, the preparation/analysis process is purge-and-trap/gas chromatography. For semivolatile organics, the QC check samples must undergo solvent extraction (see Method 3500) prior to chromatographic analysis.

8.6.4 Calculate the average recovery ($\bar{X}$) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte of interest using the four results.

8.6.5 For each analyte compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, given the QC Acceptance Criteria Table at the end of each of the determinative methods. If s and $\bar{X}$ for all analytes of interest meet the acceptance

criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in each of the QC Acceptance Criteria Tables present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.6.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.6.6.1 or 8.6.6.2.

8.6.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.6.2.

8.6.6.2 Beginning with Section 8.6.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.6.2.

8.7 The laboratory must, on an ongoing basis, spike at least one sample per analytical batch (maximum of 20 samples per batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.7.1 The concentration of the spike in the sample should be determined as follows:

8.7.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.7.2, whichever concentration would be larger.

8.7.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at the same concentration as the QC check sample (8.6.2) or 1 to 5 times higher than the background concentration determined in Section 8.7.2, whichever concentration would be larger.

8.7.1.3 For semivolatile organics, it may not be possible to determine the background concentration levels prior to spiking (e.g., maximum holding times will be exceeded). If this is the case, the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the QC check sample concentration (Section 8.6.2).

8.7.2 Analyze one unspiked and one spiked sample aliquot to determine percent recovery of each of the spiked compounds.

8.7.2.1 Volatile organics: Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.6.1) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 uL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A - B)%/T, where T is the known true value of the spike.

8.7.2.2 Semivolatile organics: Analyze one sample aliquot (extract of 1-L sample) to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.6.1) appropriate for the background concentration in the sample. Spike a second 1-L sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A - B)%/T, where T is the known true value of the spike.

8.7.3 Compare the percent recovery (p) for each analyte with the corresponding criteria presented in the QC Acceptance Criteria Table found at the end of each of the determinative methods. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than the QC check sample concentration (8.6.2), the analyst must use either the QC acceptance criteria presented in the Tables, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in the Method Accuracy and Precision as a Function of Concentration Table (appears at the end of each determinative method), substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in the same Table, substituting x' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as (100x'/T) $\pm$ 2.44(100S'/T)%.

8.7.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Section 8.8.

8.8 If any analyte fails the acceptance criteria for recovery in Section 8.7, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the

complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes given in a method must be measured in the sample in Section 8.7, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.8.1 **Preparation of the QC check standard:** For volatile organics, add 10 uL of the QC check sample concentrate (Section 8.6.1 or 8.7.2) to 5 mL of reagent water. For semivolatile organics, add 1.0 mL of the QC check sample concentrate (Section 8.6.1 or 8.7.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.7. Prepare the QC check standard for analysis following the guidelines given in Method 3500 (e.g., purge-and-trap, extraction, etc.).

8.8.2 Analyzed the QC check standard to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.8.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in the appropriate Table in each of the methods. Only analytes that failed the test in Section 8.7 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.9 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix type) as in Section 8.7, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.10 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.10.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.10.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

8.10.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

8.10.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Tables A and B of Methods 8240 and 8270, respectively. The limits given in these methods are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.10.3 must fall within those given in Tables A and B for these matrices.

8.10.5 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.10.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.11 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in the referring analytical methods were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

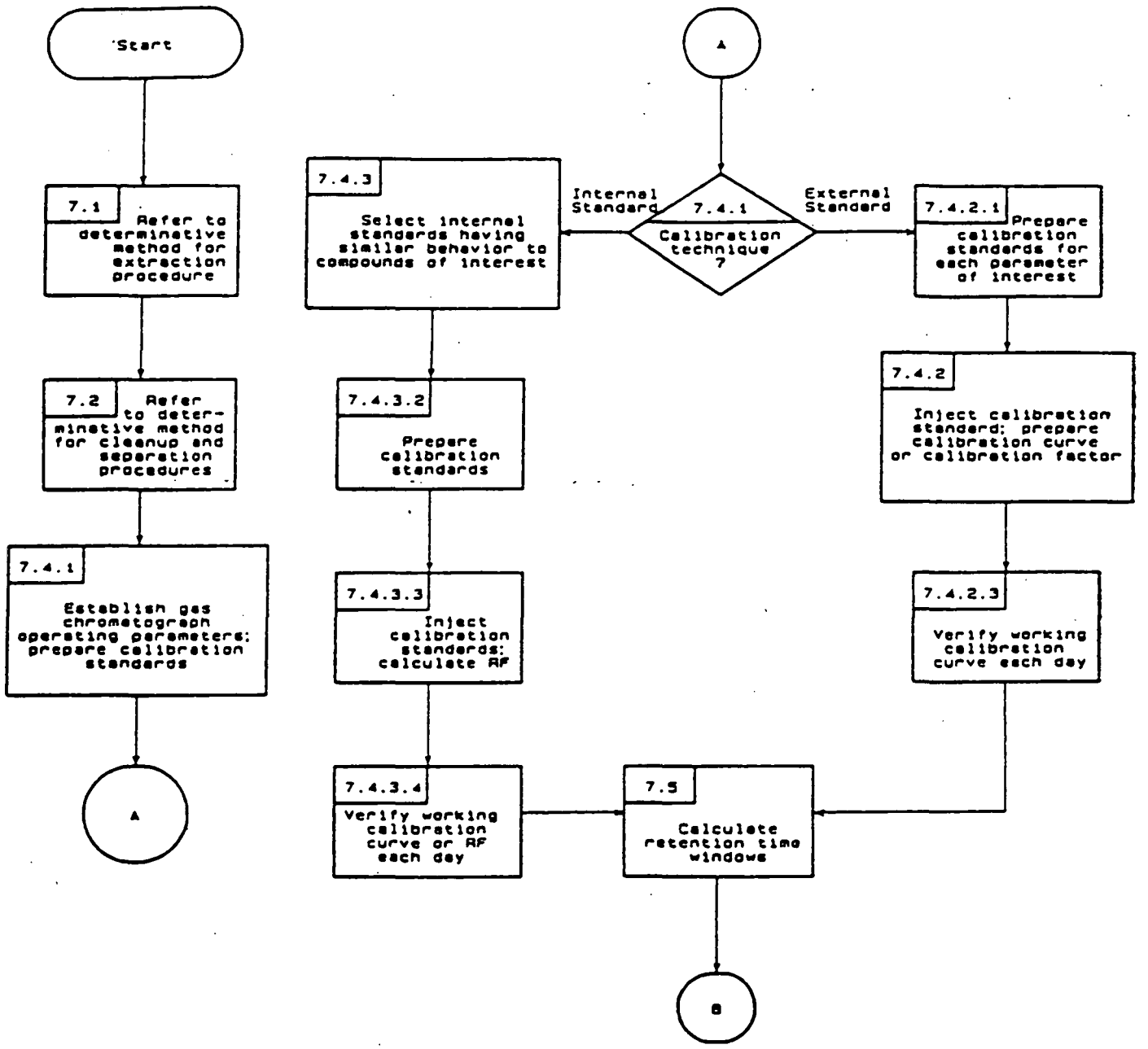
9.2 Refer to the determinative method for specific method performance information.

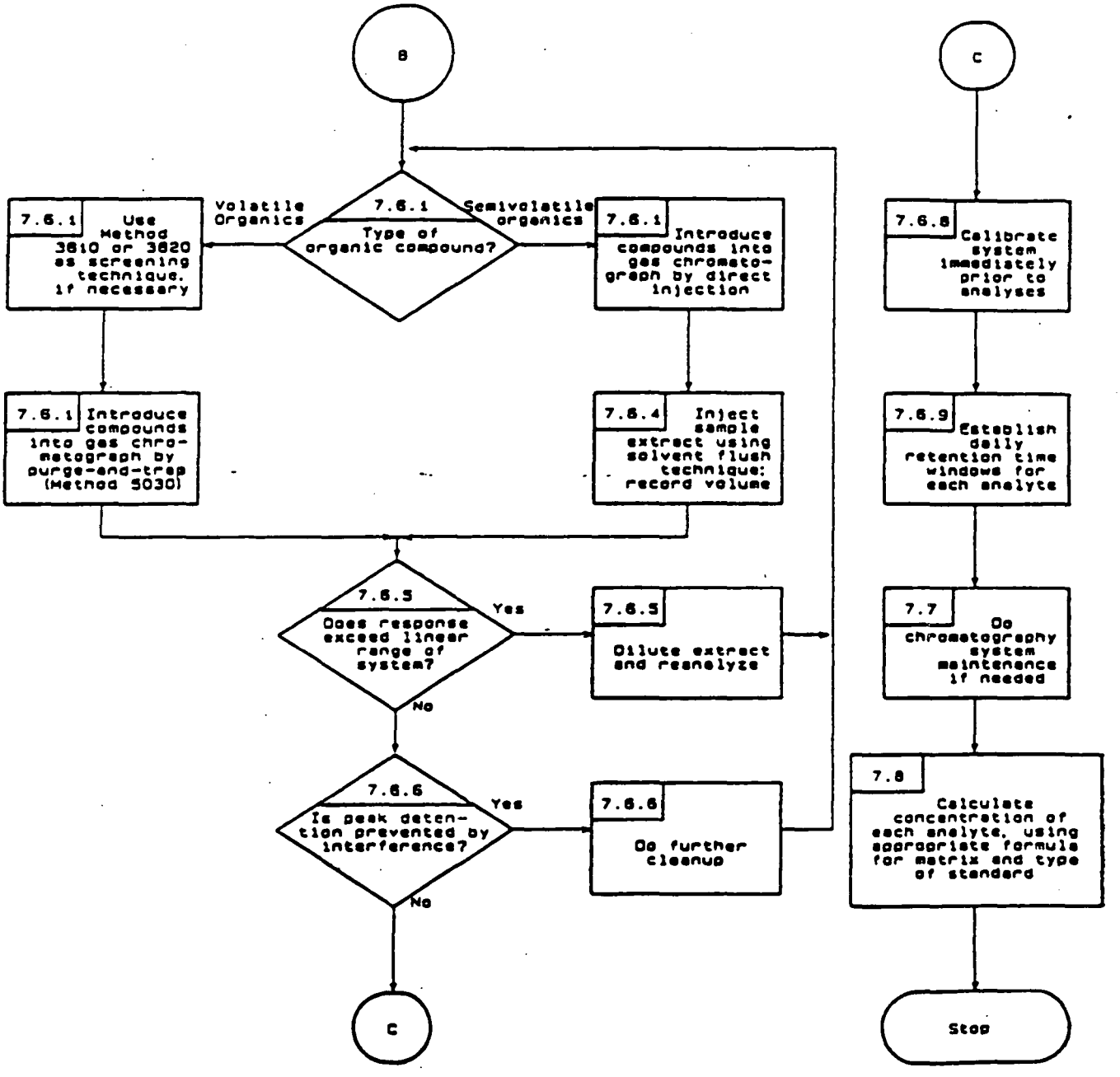
10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S. EPA 40 CFR Part 136, Appendix B. "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.


Start
7.1
Refer to determinative method for extraction procedure
7.2
Refer to determinative method for cleanup and separation procedures
7.4.1
Establish gas chromatograph operating parameters; prepare calibration standards
A
A
7.4.1
Calibration technique ?
Internal Standard
External Standard
7.4.3
Select internal standards having similar behavior to compounds of interest
7.4.3.2
Prepare calibration standards
7.4.3.3
Inject calibration standards; calculate RF
7.4.3.4
Verify working calibration curve or RF each day
7.4.2.1
Prepare calibration standards for each parameter of interest
7.4.2
Inject calibration standard; prepare calibration curve or calibration factor
7.4.2.3
Verify working calibration curve each day
7.5
Calculate retention time windows
B


B
C
7.6.1 Type of organic compound?
Volatile Organics
Semivolatile organics
7.6.1 Use Method 3810 or 3820 as screening technique, if necessary
7.6.1 Introduce compounds into gas chromatograph by purge-and-trap (Method 5030)
7.6.1 Introduce compounds into gas chromatograph by direct injection
7.6.4 Inject sample extract using solvent flush technique; record volume
7.6.5 Does response exceed linear range of system?
Yes
No
7.6.5 Dilute extract and reanalyze
7.6.6 Is peak detention prevented by interference?
Yes
No
7.6.6 Do further cleanup
C
7.6.8 Calibrate system immediately prior to analyses
7.6.9 Establish daily retention time windows for each analyte
7.7 Do chromatography system maintenance if needed
7.8 Calculate concentration of each analyte, using appropriate formula for matrix and type of standard
Stop

Method 8100 (Polynuclear Aromatic Hydrocarbons) with reference to Method 8000 (Gas Chromatography).

Sections not mentioned in the notes are to be analyzed as written.

Paragraph	Note
1.2	The gas chromatographic analysis must be able to resolve and individually quantitate perylene and benzo(a)pyrene. The column temperature and program shall be adjusted to insure resolution of perylene and benzo(a)pyrene and maximize resolution of the four compound pairs specified here.
4.1.2.2	Column 2 will be used for primary analysis and Column 1 for confirmation analysis.
5.0	Calibration shall be by use of external standards.
5.5	Surrogates and matrix spike compounds are specified in Method 3500 (modified).
7.1	Extraction/dilution shall be performed as specified in the applicable SAS and method.
7.4	All samples should be analyzed using Column 2 as specified in Section 4.1.2.2.
7.5	All samples shall be cleaned up using Method 3630.

GLT897/019.50

POLYNUCLEAR AROMATIC HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 8100 is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH). Table 1 indicates compounds that may be determined by this method.

1.2 The packed column gas chromatographic method described here cannot adequately resolve the following four pairs of compounds: anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b)fluoranthene and benzo(k)fluoranthene; and dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. The use of a capillary column instead of the packed column, also described in this method, may adequately resolve these PAHs. However, unless the purpose of the analysis can be served by reporting a quantitative sum for an unresolved PAH pair, either liquid chromatography (Method 8310) or gas chromatography/mass spectroscopy (Method 8270) should be used for these compounds.

2.0 SUMMARY OF METHOD

2.1 Method 8100 provides gas chromatographic conditions for the detection of ppb levels of certain polynuclear aromatic hydrocarbons. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID).

2.2 If interferences prevent proper detection of the analytes of interest, the method may also be performed on extracts that have undergone cleanup using silica gel column cleanup (Method 3630).

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

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

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

TABLE 1. GAS CHROMATOGRAPHY OF POLYNUCLEAR AROMATIC HYDROCARBONS[a]

Compound	Retention time (min)
Acenaphthene	10.8
Acenaphthylene	10.4
Anthracene	15.9
Benzo(a)anthracene	20.6
Benzo(a)pyrene	29.4
Benzo(b)fluoranthene	28.0
Benzo(j)fluoranthene	
Benzo(k)fluoranthene	28.0
Benzo(ghi)perylene	38.6
Chrysene	24.7
Dibenz(a,h)acridine	
Dibenz(a,j)acridine	
Dibenzo(a,h)anthracene	36.2
7H-Dibenzo(c,g)carbazole	
Dibenzo(a,e)pyrene	
Dibenzo(a,h)pyrene	
Dibenzo(a,i)pyrene	
Fluoranthene	19.8
Fluorene	12.6
Indeno(1,2,3-cd)pyrene	36.2
3-Methylcholanthrene	
Naphthalene	4.5
Phenanthrene	15.9
Pyrene	20.6

[a]Results obtained using Column 1.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 **Columns:**

4.1.2.1 Column 1: 1.8-m x 2-mm I.D. glass column packed with 3% OV-17 on Chromosorb W-AW-DCMS (100/120 mesh) or equivalent.

4.1.2.2 Column 2: 30-m x 0.25-mm I.D. SE-54 fused silica capillary column.

4.1.2.3 Column 3: 30-m x 0.32-mm I.D. SE-54 fused silica capillary column.

4.1.3 **Detector:** Flame ionization (FID).

4.2 Volumetric flask: 10-, 50-, and 100-mL, ground-glass stopper.

4.3 Microsyringe: 10-uL.

5.0 REAGENTS

5.1 Solvents: Hexane, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 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 certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with a check standard indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogates (e.g., 2-fluorobiphenyl and 1-fluoronaphthalene) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 5.3.1.1, details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and must be analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550. To achieve maximum sensitivity with this method, the extract must be concentrated to 1 mL.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set nitrogen carrier gas flow at 40-mL/min flow rate. Set column temperature at 100°C for 4 min; then program at 8°C/min to a final hold at 280°C.

7.2.2 **Column 2:** Set helium carrier gas at 20-cm/sec flow rate. Set column temperature at 35°C for 2 min; then program at 10°C/min to 265°C and hold for 12 min.

7.2.3 **Column 3:** Set helium carrier gas at 60 cm/sec flow rate. Set column temperature at 35°C for 2 min; then program at 10°C/min to 265°C and hold for 3 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques.

7.3.1 The procedure for internal or external standard calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will validate elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.4 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Section 7.8 of Method 8000 for calculation equations.

7.4.5 If peak detection and identification are prevented due to interferences, the extract may undergo cleanup using Method 3630.

7.5 Cleanup:

7.5.1 Proceed with Method 3630. Instructions are given in this method for exchanging the solvent of the extract to hexane.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene, 5 ug/mL; and any other PAH at 10 ug/mL.

8.2.2 Table 2 indicates the calibration and QC acceptance criteria for this method. Table 3 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.1 to 425 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to

the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 3.

9.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 8 x MDL to 800 x MDL with the following exception: benzo(ghi)perylene recovery at 80 x and 800 x MDL were low (35% and 45%, respectively).

9.3 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 9 - PAHs," Report for EPA Contract 68-03-2624 (in preparation).

2. Sauter, A.D., L.D. Betowski, T.R. Smith, V.A. Strickler, R.G. Beimer, B.N. Colby, and J.E. Wilkinson, "Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants," Journal of HRC&CC 4, 366-384, 1981.

3. "Determination of Polynuclear Aromatic Hydrocarbons in Industrial and Municipal Wastewaters," EPA-600/4-82-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, September 1982.

4. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

5. "EPA Method Validation Study 20, Method 610 (Polynuclear Aromatic Hydrocarbons)," Report for EPA Contract 68-03-2624 (in preparation).

6. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

7. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 2. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
Acenaphthene	100	40.3	D-105.7	D-124
Acenaphthylene	100	45.1	22.1-112.1	D-139
Anthracene	100	28.7	11.2-112.3	D-126
Benzo(a)anthracene	10	4.0	3.1-11.6	12-135
Benzo(a)pyrene	10	4.0	0.2-11.0	D-128
Benzo(b)fluoranthene	10	3.1	1.8-13.8	6-150
Benzo(ghi)perylene	10	2.3	D-10.7	D-116
Benzo(k)fluoranthene	5	2.5	D-7.0	D-159
Chrysene	10	4.2	D-17.5	D-199
Dibenzo(a,h)anthracene	10	2.0	0.3-10.0	D-110
Fluoranthene	10	3.0	2.7-11.1	14-123
Fluorene	100	43.0	D-119	D-142
Indeno(1,2,3-cd)pyrene	10	3.0	1.2-10.0	D-116
Naphthalene	100	40.7	21.5-100.0	D-122
Phenanthrene	100	37.7	8.4-133.7	D-155
Pyrene	10	3.4	1.4-12.1	D-140

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 610. These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.52C+0.54	0.39$\bar{X}$+0.76	0.53$\bar{X}$+1.32
Acenaphthylene	0.69C-1.89	0.36$\bar{X}$+0.29	0.42$\bar{X}$+0.52
Anthracene	0.63C-1.26	0.23$\bar{X}$+1.16	0.41$\bar{X}$+0.45
Benzo(a)anthracene	0.73C+0.05	0.28$\bar{X}$+0.04	0.34$\bar{X}$+0.02
Benzo(a)pyrene	0.56C+0.01	0.38$\bar{X}$-0.01	0.53$\bar{X}$-0.01
Benzo(b)fluoranthene	0.78C+0.01	0.21$\bar{X}$+0.01	0.38$\bar{X}$-0.00
Benzo(ghi)perylene	0.44C+0.30	0.25$\bar{X}$+0.04	0.58$\bar{X}$+0.10
Benzo(k)fluoranthene	0.59C+0.00	0.44$\bar{X}$-0.00	0.69$\bar{X}$+0.10
Chrysene	0.77C-0.18	0.32$\bar{X}$-0.18	0.66$\bar{X}$-0.22
Dibenzo(a,h)anthracene	0.41C-0.11	0.24$\bar{X}$+0.02	0.45$\bar{X}$+0.03
Fluoranthene	0.68C+0.07	0.22$\bar{X}$+0.06	0.32$\bar{X}$+0.03
Fluorene	0.56C-0.52	0.44$\bar{X}$-1.12	0.63$\bar{X}$-0.65
Ideno(1,2,3-cd)pyrene	0.54C+0.06	0.29$\bar{X}$+0.02	0.42$\bar{X}$+0.01
Naphthalene	0.57C-0.70	0.39$\bar{X}$-0.18	0.41$\bar{X}$+0.74
Phenanthrene	0.72C-0.95	0.29$\bar{X}$+0.05	0.47$\bar{X}$-0.25
Pyrene	0.69C-0.12	0.25$\bar{X}$+0.14	0.42$\bar{X}$-0.00

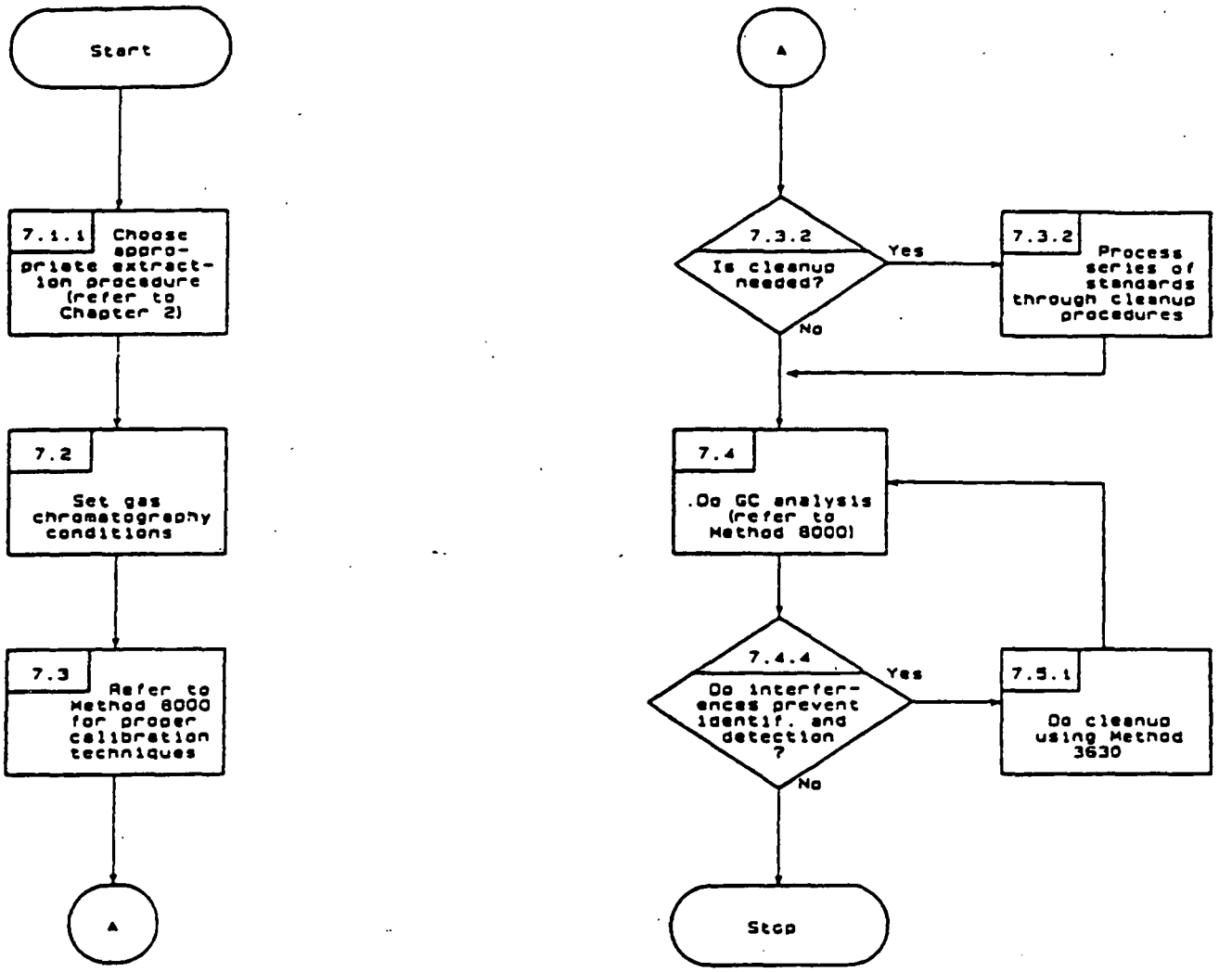
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.


Start
7.1.1 Choose appropriate extraction procedure (refer to Chapter 2)
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
A
A
7.3.2 Is cleanup needed?
Yes
No
7.3.2 Process series of standards through cleanup procedures
7.4 Do GC analysis (refer to Method 8000)
7.4.4 Do interferences prevent identif. and detection ?
Yes
No
7.5.1 Do cleanup using Method 3630
Stop

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

SAS Number
[ ]

SPECIAL ANALYTICAL SERVICES
Regional Request

[X] **Regional Transmittal** [ ]**Telephone Request**

A. EPA Region and Site Name: Moss-American/Region V

B. Regional Representative: Jan Pels

C. Telephone Number: (312) 353-2720

D. Date of Request:

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

1. General description of analytical service requested:
2,3,7,8-specific tetrachlorinated dibenzodioxin and dibenzofuran, total tetra through octa polychlorinated dibenzodioxins and dibenzofurans, and % moisture.
DO NOT SUBCONTRACT WITHOUT PRIOR REGIONAL APPROVAL

---

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or Soil and sediments; and whether low, medium, or high concentrations):
Analyze seventeen (17) sediment samples for chlorinated dibenzodioxins and dibenzofurans.

---

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

Superfund Remedial

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment:
Daily by overnight courier

6. Approximate number of days results required after lab receipt of samples:
Extract within 5 days of VTSR and analyze within 40 days.
Data due within 45 days

---

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
Extraction: Benzene Soxhlet as described in Anal. Chem. 1980, **52**, 2045-2054 (Appendix I).
Clean-up: HPLC/RPHPLC as described in above reference or Dioxin IFB WA86K357 options including carbon column cleanup as needed to meet surrogate percent recovery limits. (Appendix II)
Instrument: Use HRMS or LRMS to meet target detection limits.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
(1) Determine and report % moisture (use CLP IFB protocol - Appendix III)
(2) Report all data on a dry weight basis.
(3) Stir soil samples for 30 seconds before removing aliquot.
(4) Quantitation and standards requirements. (Appendix IV)
(5) MUST monitor for the masses of the polychlorinated diphenyl ether interferences in all furan isomer groups.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of Custody documentation, etc.). If not completed, format of results will be left to program discretion.
Appendix V for deliverables
Appendix VI for suggested data report format.
Remember to report % moisture.

---

10. Other (use additional sheets or attach supplementary information, as needed):
DO NOT SUBCONTRACT WITHOUT PRIOR REGIONAL APPROVAL.

11. Name of sampling/shipping contact:

Phone: Dave Shekoski
(414) 272-2426

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (+/- % or conc.)
2,3,7,8-TCDD/TCDF	5 ppt	
Total TCDD/TCDF	5 ppt	
Total Penta CDD/CDF	20 ppt	
Total Hexa CDD/CDF	20 ppt	
Total Hepta CDD/CDF	20 ppt	
OCDD/OCDF	50 ppt	

II. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (+/- % or conc.)
Method Blank	1 per 20 samples or set	< target Det. Lim.
In lab matrix spike		see attachment
Matrix spike duplicates		see attachment
Surrogate spikes	in every sample	

III. Action Required if Limits are Exceeded:

1. Follow procedures specified in the Dioxin IFB WA-86K357 (Appendix II)

2. Call Region V if problem persists. (Frank Thomas, (312)-886-5482)

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

11. Surrogate, Duplicate and Matrix Spike Limits

A. In Laboratory Matrix Spike

Compound	Level		Recovery Limits
2378-TCDD	≤ 50 ppt		70 - 130%
2378-TCDF	≤ 50 ppt		70 - 130%
Penta CDD/CDF	≤ 200 ppt	*	40 - 160%
Hexa CDD/CDF	≤ 200 ppt	*	40 - 160%
Hepta CDD/CDF	≤ 200 ppt	*	40 - 160%
OCDD/OCDF	≤ 500 ppt	*	40 - 160%

* At least one isomer from each of these classes should be used in the spike solution.

B. Surrogate Spikes (required in every sample)

Surrogate	Level [a]	Recovery Limits
$^{37}Cl_4$ 2378-TCDD	5 ng	50 - 115%
$^{13}C_{12}$ ~~or $^{37}Cl_4$ 2378-TCDF~~ PeCDD	5 ng	50 - 115%
~~$^{37}Cl_4$ OCDD~~ or $^{13}C_{12}$-HpCDD $^{13}C_{12}$-HxCDD	10 - 20 ng	40 - 110%

[a]Added to 10g sample

C. In Matrix Spike Duplicate

Class	RPD Limit
2378- TCDD/TCDF	≤ 30% RPD
Penta CDD/CDF	≤ 60% RPD
Hexa CDD/CDF	≤ 60% RPD
Hepta CDD/CDF	≤ 60% RPD
OCDD/OCDF	≤ 30% RPD

Determination of Tetra-, Hexa-, Hepta-, and Octachlorodibenzo-*p*-dioxin Isomers in Particulate Samples at Parts per Trillion Levels

L. L. Lamparski* and T. J. Nestrick

Analytical Laboratories, 574 Building, Dow Chemical U.S.A., Midland, Michigan 48640

An analytical procedure is presented which permits the isomer-specific determination of tetra-, hexa-, hepta-, and octachlorodibenzo-*p*-dioxins simultaneously at parts per trillion concentrations. Typical data are presented to establish its applicability on a variety of environmental particulate samples. The use of a highly specific sample clean-up procedure based on multiple chromatographies is shown to permit the isomer-specific determination of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2378-TCDD) by packed-column gas chromatography–low-resolution mass spectrometry in the presence of any or all other TCDD isomers.

The determination of parts per trillion (10^{-12} g/g, pptr) concentrations of chemical residues generally requires the use of either highly selective sample purification procedures and/or very specific detectors (*1*, *2*). As detection limits are lowered, the number of possible interferences present at significant concentrations increases dramatically (*3*). Donaldson (*4*) has surmized that every known organic chemical could be detected in water at a level of 10^{-15} g/g or higher. Similarly, considering an analysis at the 10 pptr concentration level in a sample matrix that is 99.9% pure, interferences from as many as 10^5 compounds at concentrations 10^3 times higher than the component of interest are possible. Naturally the addition of interferences from sources other than the sample matrix can make this task formidable. Such contamination of laboratory reagents by a multitude of compounds has been reported (*5–19*). Indeed, in some cases, the controlling factor in determining the limit of detection (LoD) for a given analysis is not the instrumental sensitivity of the detector but the apparent response observed in reagent blanks (*20–22*).

This paper reports the development of an analytical procedure which permits the isomer-specific determination of 2378-TCDD at low parts per trillion concentrations, even in matrices that have been intentionally fortified with equivalent amounts of each of the other 21 TCDD isomers. Higher chlorinated dioxins, including hexachlorodibenzo-*p*-dioxins (HCDDs, 10 possible isomers), heptachlorodibenzo-*p*-dioxins (H_7CDDs, 2 possible isomers), and octachlorodibenzo-*p*-dioxin (OCDD), can also be determined at low parts per trillion levels by using this technique. In regards to the isomer-specific determination of 2378-TCDC, the other 21 TCDD isomers may also be considered as possible interferences. Several publications have recently appeared which demonstrate CDD determination capabilities but do not provide complete TCDD isomer specificity (*23–32*).

EXPERIMENTAL SECTION

Reagents. The preparation of 44% concentrated sulfuric acid on silica, 10% silver nitrate on silica, basic alumina, and purified nitrogen (Femtogas) have been described (*1*).

Silica. This adsorbent is prepared from chromatographic grade silicic acid as described for the preparation of 44% sulfuric acid on silica (*1*).

33% 1 M Sodium Hydroxide on Silica. The silica support is prepared as described (*1*). Activated silica is weighed into an appropriately sized glass bottle. On the basis of the support weight, the amount of 1 M aqueous sodium hydroxide necessary to yield a reagent containing 33% by weight is added in a stepwise fashion with shaking to produce a uniformly coated, free-flowing powder.

Chemicals and Solvents. All solvents used are Burdick and Jackson, distilled-in-glass quality. Laboratory chemicals (H_2SO_4, $AgNO_3$, NaOH) are ACS reagent grade. These materials are tested by subjecting them to the analytical procedure to verify the absence of contamination. Spectrophotometric grade Gold-label *n*-hexadecane was obtained from Aldrich Chemical Co. (Milwaukee, WI) and was purified by passage through basic alumina.

Expendables. Pyrex glass wool, silica boiling stones, and disposable pipettes are cleaned before use. Glass wool and boiling stones are Soxhlet extracted ~1 h consecutively with the following solvents: methanol, chloroform + benzene (1:1 by volume), benzene, and methylene chloride. They are then dried in a hot air oven at ~160 °C for ~1 h. Disposable pipettes are cleaned ultrasonically in deionized water and then methanol and finally methylene chloride prior to drying at ~160 °C. Final sample residues are stored in Reacti-Vials obtained from Pierce Chemical Co. (Rockford, IL). The vials are cleaned by washing with detergent and water and then boiled sequentially in benzene + chloroform + methanol (1:1:1 by volume), benzene + chloroform (1:1 by volume), benzene, and finally methylene chloride. They are air-dried and again rinsed with methylene chloride immediately before use.

Dioxin Standards. The primary standard of 2378-TCDD was prepared by W. W. Muelder (Dow Chemical Co.) and its structure was confirmed by single-crystal X-ray diffraction techniques (*33*). Purity was assessed at 98% by mass spectrometry. Standards of other TCDD isomers were synthesized and isolated as previously described (*34*). Primary standards of 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (1234678-H_7CDD) and OCDD were synthesized by H. G. Fravel and W. W. Muelder (Dow Chemical Co.). A standard containing two HCDD isomers was prepared by Aniline (*35*). Standards of 1234679-H_7CDD and the 10 HCDD isomers were synthesized and isolated in a manner similar to that reported for TCDDs (*34*). Isotope-enriched ^{13}C-2378-TCDD and ^{13}C-123478-HCDD were synthesized by A. S. Kende (University of Rochester, Rochester, NY). Mass spectrometric analysis indicated these standards to be 86 atom % and 43 atom % ^{13}C, respectively. Perchlorination of the ^{13}C-2378-TCDD provided ^{13}C-OCDD.

Apparatus. *Reverse-Phase High-Performance Liquid Chromatography (RP-HPLC).* Residues containing chlorinated dioxins are injected into the RP-HPLC system: column, two 6.2 × 250 mm Zorbax-ODS (DuPont Instruments Division, Wilmington, DE) columns in series; isocratic eluent, methanol at 2.0 mL/min; pump, Altex Model 110A; column temperature, 50 °C; UV detector, Perkin-Elmer Model LC-65T liquid chromatographic column oven and detector operated at 0.02 aufs at 235 nm; injector, Rheodyne Model 7120 with 50-μL sample loop.

Normal-Phase Adsorption High-Performance Liquid *Chromatography (Silica-HPLC).* Residues containing TCDDs are injected into the silica-HPLC system: column, two 6.2 × 250 mm Zorbax-SIL (DuPont Instruments Division) columns in series; isocratic eluent, hexane at 2.0 mL/min; pump, Altex Model 110A; column temperature, ambient; UV detector, Laboratory Data Control Model 1204 variable-wavelength detector at 0.05 aufs at 235 nm; injector, Rheodyne Model 7120 with 100-μL sample injection loop. The columns were activated by the procedure of Bredeweg et al. (*36*).

Packed-Column Gas Chromatography–Low-Resolution Mass Spectrometry (GC-LRMS). Chlorinated dioxin quantification

Reprinted from Analytical Chemistry, 1980, 52, 2045.

was accomplished by GC-LRMS using a Hewlett-Packard Model 5992-A operating in the selected ion mode (SIM) at unit resolution: column, 2 mm i.d. × 210 cm silylated glass; packing, 0.60% OV-17 silicone + 0.40% Poly S-179 on 80/100 mesh Permabond Methyl Silicone-10 cycle (HNU Systems Inc., Newton, MA); injection port temperature, 280 °C on-column; carrier gas, helium at 14 cm^3/min; separator, single stage glass jet operating at column temperature; electron energy, 70 eV. TCDD analyses conditions: column temperature, 246 °C isothermal; ions monitored, native TCDDs at m/e 320, 322, and 324, and ^{13}C-2378-TCDD internal standard at m/e 332. Higher chlorinated dioxin analyses conditions: column temperature, programmed from 230 to 300 °C at 10 °C/min and hold at maximum; ions monitored, native HCDDs at m/e 388, 390, and 392, native H_7CDDs at m/e 422, 424, and 426, and native OCDD at m/e 458, 460, and 462. ^{13}C-123478-HCDD and ^{13}C-OCDD are monitored at m/e 398 and 470, respectively.

Environmental Particulate Samples. *Industrial Dust.* Particulates were removed from the air intake filtration system from a research building located in Midland, MI.

Electrostatically Precipitated Fly Ash. Particulates were collected from the ash-removal system associated with the electrostatic precipitator on the Nashville Thermal Transfer Corp. refuse incinerator located in Nashville, TN.

Activated Municipal Sludge. Representative samples were removed from the center of a commercially purchased 20-kg bag of Milwaukee Milorganite.

Urban Particulate Matter. Standard Reference Material No. 1648 was obtained from the National Bureau of Standards (NBS).

European Fly Ash. Particulate emissions from a municipal trash incinerator were collected on filter paper by a nonisokinetic sampling procedure. The location of the sampling port was downstream from the electrostatic precipitator. This incinerator was not operated to recover energy for power generation.

Sample Preparation. Prior to GC-LRMS SIM quantification, the sample is prepared by using five basic steps: (1) chlorinated dioxins removal from the matrix via hydrocarbon extraction, (2) chemically modified adsorbent treatment of the extract to remove easily oxidizable species, (3) adsorbent treatment to remove common chemical interferences, (4) RP-HPLC residue fractionation to remove residual chemically similar interferences and to separate dioxins present into groups according to their degree of chlorination, and (5) silica-HPLC refractionation of the RP-HPLC TCDD fractions to provide a second high-efficiency chromatographic separation having different selectivity to remove residual interferents and to permit TCDD isomer specificity.

An appropriately sized all-glass Soxhlet extraction apparatus equipped with a water-cooled condenser, a 43 × 125 mm glass thimble with coarse frit, a 250-mL boiling flask, and a temperature-controlled heating mantle is assembled. Each of the parts is thoroughly scrubbed with an aqueous detergent solution, rinsed with deionized water followed by acetone, methanol, and methylene chloride, and finally air-dried. Depending on the particulate sample size (larger samples require most), 5–15 g of silica is charged into the thimble followed by a plug of glass wool large enough to cover the silica bed completely. The assembled system (thimble installed) is charged with benzene (~250 mL) and allowed to reflux at a recycle rate of ~20 mL/min for a minimum period of 2 h. Following this preextraction period, the system is permitted to cool and the total benzene extract is discarded. The extraction thimble is removed and allowed to drain completely on a clean wire stand in a fume hood. The glass wool plug is removed with clean forceps while a representative particulate sample, ranging from 50 mg for filtered airborne particulates to 100 g for heavy soils, is quickly charged on top of the silica bed. The glass wool plug is replaced and the thimble returned to the Soxhlet extractor body. At this time aliquots of isooctane internal standard solutions containing isotopically labeled 2378-TCDD, 123478-HCDD, and OCDD are introduced directly into the particulates bed. The system is recharged with fresh benzene and exhaustively extracted at the rate previously described for a minimum period of 16 h. Each sample or set should have at least one system treated as described for the sample to serve as a reagent blank.

Upon completion of the prescribed extraction period, the flask containing the benzene extract is removed and fitted with a three-

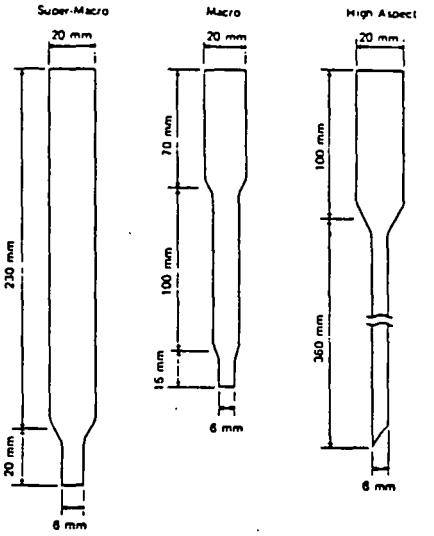


Figure 1. Liquid chromatographic clean-up columns.

to six-stage Snyder distillation column. The volume of the extract solution is then reduced by atmospheric pressure distillation of the benzene solvent to a final volume of approximately 25 mL. The concentrated benzene extract is then diluted with a roughly equal volume of hexane when cool.

Bulk matrix (benzene extractables other than CDDs) removal is accomplished by passing the residue extract solution through a Super-Macro chromatographic column (see Figure 1) prepared as follows. The column is thoroughly washed and dried just prior to use via the same procedure described for the Soxhlet extractor. A glass wool plug is inserted into the end of the column to serve as a bed support, and the following reagents are then carefully weighed directly into the column: 1.0 g of silica (bottom layer), 2.0 g of 33% 1 M sodium hydroxide on silica, 1.0 g of silica, 4.0 g of 44% concentrated sulfuric acid on silica, and 2.0 g of silica (top layer). The freshly packed column is then immediately prewashed with 30 mL of hexane and the effluent discarded. The residue extract is then passed through the column followed by 3 × 5-mL hexane rinses of the boiling flask vessel. Following these rinses an additional 30 mL of hexane is passed through the column. The total effluent is collected in a 150-mL beaker and then evaporated to dryness under a stream of Femtogas nitrogen. A single drop of *n*-hexadecane (~25 mg) is added to the reagent blank prior to its evaporation to dryness as a means of improving internal standard recovery.

Common chemical interferences are removed by passage of the residue through a dual column system consisting of a top Macro chromatographic column draining into a bottom High Aspect column. (See Figure 1.) Each of these columns is cleaned as previously described and a glass wool bed support inserted just prior to use. The Macro column is packed with 1.5 g of 10% silver nitrate on silica and prewashed with 15 mL of hexane prior to use. The High Aspect column is packed with 5.0 g of basic alumina. When the top Macro column prewash has drained, it is positioned over the High Aspect column reservoir. The sample residue is dissolved in ~15 mL of hexane and introduced into the top column followed by 3 × 5-mL hexane beaker rinses. Following the rinses, an additional 30 mL of hexane is passed through the system. When drained, the top column is discarded. After the hexane has drained to bed level in the High Aspect column, 50 mL of 50% (v/v) carbon tetrachloride in hexane is passed through. The total effluent to this point can be discarded. A 25-mL glass vial (cleaned same as chromatographic columns) is used to collect the total effluent after 22.5 mL of 50% (v/v) methylene chloride in hexane is introduced into the column. When elution is complete this fraction which contains chlorinated dioxins is evaporated to dryness under a stream of Femtogas nitrogen (*1*).

RP-HPLC fractionation of the residue is initiated by calibration of the appropriate collection zones for TCDDs, HCDDs, H_7CDDs, and OCDD. This is accomplished by injecting a calibration

standard containing approximately 10–20 ng each: 2378-TCDD, HCDD(s), $H_7CDD(s)$, and OCDD in no more than 30 μL of chloroform. In accordance with the chromatogram obtained, appropriate collection zones are established for each of these species (see Discussion section). Following calibration, the injector is rinsed with copious quantities of chloroform, to include multiple consecutive injections of 50 μL of chloroform into the column to ensure that no residual chlorinated dioxins remain.

The residue is prepared for RP-HPLC fractionation by quantitative transfer to a 0.3-mL Reacti-Vial. Quantitative injection requires complete residue solubility in 30 μL or less of chloroform. Larger injections of chloroform into this RP-HPLC system severely reduce column efficiency. An aliquot of no more than 30 μL can be fractionated if the sample residue requires greater amounts of chloroform to be dissolved. Appropriate chlorinated dioxin fractions are collected in 25-mL volumetric flasks, equipped with ground glass stoppers, containing ~1 mL of hexane. The chlorinated dioxins are recovered by addition of 2% (w/v) aqueous sodium bicarbonate. The hexane layer is transferred to a 5-mL glass vial and the aqueous phase is extracted three additional times with ~1 mL of hexane. The combined extracts are then evaporated to dryness under a stream of Femtogas nitrogen. HCDD, H_7CDD, and OCDD fractions are quantitatively transferred to 0.3-mL Reacti-Vials and diluted to appropriate volumes for determination by GC-LRMS.

Regarding the case for an isomer-specific 2378-TCDD determination, additional silica-HPLC fractionation of the RP-HPLC 2378-TCDD fraction is required (see Discussion section). Calibration of the appropriate collection zone is accomplished by injecting approximately 10 ng of 2378-TCDD into the silica-HPLC in 60–80 μL of hexane and monitoring the chromatogram obtained. Adequate isomer specificity is obtained when the silica-HPLC columns are sufficiently dry so as to provide a 2378-TCDD retention time ranging from a minimum of 12.5 min to maximum of 17 min (*24*). Following injection of the residue fraction, the chromatogram is monitored and the appropriate 2378-TCDD fraction is collected in a 5-mL glass vial. This fraction is then evaporated to dryness under a stream of Femtogas nitrogen and diluted to appropriate volume for determination by GC-LRMS. This procedure can also be used to collect other TCDD isomers as described in the Discussion section; see Figure 2.

DISCUSSION

The purpose of this paper is to demonstrate the feasibility of using a single multiple-step procedure to accomplish the isomer-specific determination of TCDDs, HCDDs, H_7CDDs, and OCDD at low part per trillion concentrations in a variety of environmental particulate samples. There were two prerequisites for our development of the methodology. First, the sample cleanup must be capable of recovering each of the listed chlorinated dioxin (CDD) groups from a single sample and from a single workup. And second, all procedures must use the least sophisticated and most reliable instrumentation possible so that such analyses could be conducted in the greatest number of analytical facilities. These prerequisites have determined the means by which the described analyses can be accomplished. That is, a neutral or acid extraction procedure must be used. Any treatment of either the sample or its extracts with strong bases is known to cause degradation of the higher chlorinated dioxins (*21*, *37*). In accordance with ease of handling and the general solubility characteristics of higher chlorinated dioxins (least soluble species), continuous benzene extraction was found to be adequate for all particulate samples examined. The selection of packed-column gas chromatography–low-resolution mass spectrometry as opposed to capillary column gas chromatography–high-resolution mass spectrometry represents our attempt to use the least sophisticated instrumentation for CDD determination. Because packed-column GC-LRMS is inherently more subject to possible interference than capillary column GC-HRMS, a more rigorous sample preparation is required. The approach of combining classical extraction and adsorbent clean-up techniques with consecutive RP-HPLC and silica-HPLC residue

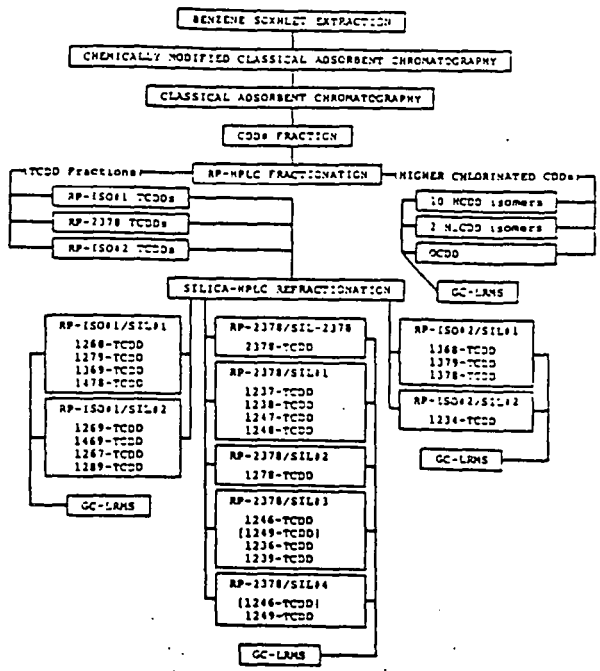


Figure 2. Block diagram for CDD sample preparation.

fractionations can be one solution to this problem. Under these circumstances a significant portion of the method capabilities to prevent MS interferences during the identification and quantification of CDDs is relegated to the cleanup rather than to the final gas chromatographic separation. This can be advantageous when dealing with highly contaminated samples because the chromatographic capacity of the clean-up steps is usually much greater than that of the GC column, especially when capillaries are used. In addition, this approach incorporates the consecutive RP-HPLC and silica-HPLC steps that we have published for the separation and isolation of the 22 TCDD isomers (*34*). Their described application in this procedure permits the analyst to predetermine which possible TCDD isomers can be present in a given residue fraction. Hence, the necessity of using a capillary GC column to obtain improved TCDD isomer separations is eliminated. This capability may be of utmost importance as the authors are not aware of any published data suggesting that all 22 TCDD isomers can be separated simultaneously using a single capillary GC column. The described methodology will address this problem.

It is to be understood that this procedure has been developed and used for survey purposes on a variety of different environmental particulates. A complete method validation including controls, fortifications, and replicates would be required for each specific matrix before its absolute degree of reliability can be established. The inclusion of isotopically enriched TCDD, HCDD, and OCDD internal standards provide a reasonable degree of reliability under the circumstances of its described uses.

The samples 1.0 g of NBS urban particulate matter, 1.0 g of industrial dust, 1.0 g of electrostatically precipitated fly ash from a municipal burner (fly ash), 16.7 g of Milorganite, and 0.3968 g of European flyash were Soxhlet extracted with benzene for ~16 h and the resulting residues processed through the preliminary liquid chromatographic clean-up steps. Each sample, to include a reagent blank, was fortified with 5–20 ng of isotopically enriched internal standard CDDs (^{13}C enrichment) prior to analysis. After transfer to a 0.3-mL Reacti-Vial and evaporation of the solvent, all samples yielded a visible white residue. Each of these was then quantitatively

Table I. TCDD Isomer RP-HPLC Fractionation Scheme and Specific Retention Indices

TCDD isomer	RP-HPLC abs RT,[a] min	silica-HPLC rel RT[b]	GC packed column rel RT[c]
	RP-Iso No. 1 Fraction		
1269	11.6-13.0	1.702	0.998
1469	11.6-13.0	1.497	0.912
1267/1289	12.2-12.9	1.623	1.081
	12.2-12.9	1.795	1.200
1268/1279	13.3-13.9	1.238	0.956
	13.3-13.9	1.291	1.065
1369/1478	13.3-13.9	1.220	0.802
	13.3-13.9	1.340	0.907
	RP-2378 Fraction		
1246/1249	13.7-14.5	1.328	0.896
	13.7-14.5	1.411	0.898
2378	13.8-14.5	1.000	1.006[d]
1236/1239	13.8-14.4	1.356	1.037
	14.4-15.2	1.350	0.969
1278	14.0-14.7	1.288	0.893
1237/1238	14.0-15.0	1.100	0.979
	14.0-15.0	1.128	0.990
1247/1248	14.2-15.1	1.154	0.854
	14.2-15.1	1.199	0.857
	RP-Iso No. 2 Fraction		
1378	14.9-15.7	1.000	0.858
1379	14.9-15.9	0.940	0.771
1368	15.9-16.8	0.977	0.729
1234	15.8-16.8	1.248	0.960

[a] RP-HPLC abs RT = absolute retention time (±0.1 min) to collect peak. [b] Silica-HPLC rel RT = retention time relative to 2378-TCDD (±0.010). [c] GC-packed column rel RT = retention time relative to ^{13}C-2378-TCDD (±0.005). [d] Native 2378-TCDD elutes slightly later than ^{13}C-2378-TCDD.

subjected to reverse-phase high-performance liquid chromatography fractionation. The resultant liquid chromatograms monitored by a UV detector at 235 nm ($\sim\lambda_{max}$ for TCDDs) and 0.02 aufs are shown in Figure 3b–f. Shown in Figure 3a is the chromatogram obtained for a CDD calibration standard by RP-HPLC. Although the appropriate CDD collection zones, denoted by dotted lines, were initially established by individual injections of 22 TCDD isomers, 10 HCDD isomers, 2 H_7CDD isomers, and OCDD, we routinely compute their location from the observed retention times of only a few selected species. The specific RP-HPLC retention indices for TCDDs are given in Table I and those for HCDDs, H_7CDDs, and OCDD are listed in Table II.

As indicated, all 22 TCDD isomers can be fractionated from a sample residue by collecting the column effluent beginning at ~11.5 and ending at ~17.0 min. The initial stage of TCDD isomer specificity is achieved by collecting the 22 isomers in three separate fractions as shown. TCDD Iso No. 1 (RP-HPLC TCDD isomer fraction no. 1) can contain the following isomers: 1269-, 1469-, 1267-, 1289-, 1268-, 1279-, 1369-, and 1478-TCDD. The TCDD 2378 fraction contains 1246-, 1249-, 2378-, 1236-, 1239-, 1278-, 1237-, 1238-, 1247-, and 1248-TCDD. TCDD Iso No. 2 contains the remaining four isomers: 1378-, 1379-, 1368-, and 1234-TCDD. Preliminary evidence, gained by fortifying samples with roughly equal amounts of all 22 TCDD isomers at approximately the 150 pptr concentration level, has indicated that three of the possible isomers in TCDD Iso No. 1 must be sacrificed in order to ensure quantitative collection of 2378-TCDD in the following fraction. This consequence will be discussed later. Its occurrence is related to the RP-HPLC retention times for the isomers: 1369-TCDD, 1478-TCDD, and one of the pair 1268- or 1279-TCDD having Sil rel RT 1.238 (normal-phase silica HPLC retention time relative to 2378-TCDD). Their retention times are very close to the fraction boundary separating Iso No. 1 and 2378 and are split rather irreproducibly between these fractions. Although these isomers do not necessarily interfere with the quantitation of the isomers expected to the present in the TCDD 2378 fraction, their quantitation essentially becomes impossible. For cases where quantitation of these three TCDDs is required, a second aliquot of sample residue can be fractionated by RP-HPLC in such a manner so as to expand the Iso No. 1 fraction to ensure their collection.

Table II. HCDDs, H_7CDDs, and OCDD Retention Indices

CDD isomer	silica-HPLC rel RT[a]	RP-HPLC abs RT[b]	GC-packed column rel RT[c]
HCDDs			
123469-HCDD	1.081	19.28	0.954
123467-HCDD	1.192	19.47	1.077
124679/124689-HCDD	0.958	19.62	0.805
124679/124689-HCDD	0.972	19.70	0.806
123678/123789-HCDD	1.060	20.07	1.103
123679/123689-HCDD	0.970	20.20	0.903
123679/123689-HCDD	1.039	20.28	0.908
123678/123789-HCDD	0.974	20.85	1.016
123478-HCDD	0.941	21.02	1.006[d]
123468-HCDD	0.890	21.87	0.861
H_7CDDs			
1234679-H_7CDD		24.00	
1234678-H_7CDD		24.65	
OCDD		29.40	

[a] Silica-HPLC rel RT = retention time relative to 2378-TCDD (±0.010). [b] RP-HPLC abs RT = absolute retention (±0.1 min) at peak maximum. [c] GC packed column rel RT = retention time relative to ^{13}C-123478-HCDD. [d] Native 123478-HCDD elutes slightly later than ^{13}C-123478-HCDD.

The 10 HCDD isomers are collected in accordance with Figure 3 and Table II. Although isomer-specific HCDD determinations are possible by using essentially the same chromatography procedures described for TCDDs (i.e., RP-HPLC → silica-HPLC → GC), we have not yet applied this system to samples. Similarly, the two H_7CDD isomers are collected in a single fraction, as is OCDD.

The RP-HPLC residue fractionation chromatograms in Figure 3 are typical of those associated with particulate samples. The presence of higher chlorinated species, such as H_7CDDs and OCDD, can often be observed at this point in the analysis. Although the UV detector has been adjusted for maximum sensitivity for TCDDs, under these conditions a detectable response for HCDDs, H_7CDDs, and OCDD is obtained for approximately 5 ng. Similarly, heptachlorodibenzofurans (H_7CDFs) and octachlorodibenzofuran (OCDF) may also be observed in the RP-HPLC fractionation. Because of the lack of availability of authenticated chlorinated dibenzofuran (CDFs) standards, we have made no attempt to quantitate these species. Via collection of appropriate RP-HPLC fractions, and capillary GC-EC and GC-LRMS, we have established the possible presence of four H_7CDF isomers and OCDF in a variety of particulate samples.

Refractionation of the RP-HPLC TCDD fractions via normal-phase HPLC (silica-HPLC) is the final stage of the sample cleanup prior to GC-LRMS analysis. Normally monitoring of these chromatograms with a UV detector at 0.05 aufs and 235 nm does not produce observable peaks with the exception of the ^{13}C-2378-TCDD internal standard. For this reason example chromatograms are omitted. Table I lists the individual TCDD isomers contained in each RP-HPLC TCDD fraction. Included are the RP-HPLC, silica-HPLC, and GC packed column retention indices for each species. By use of

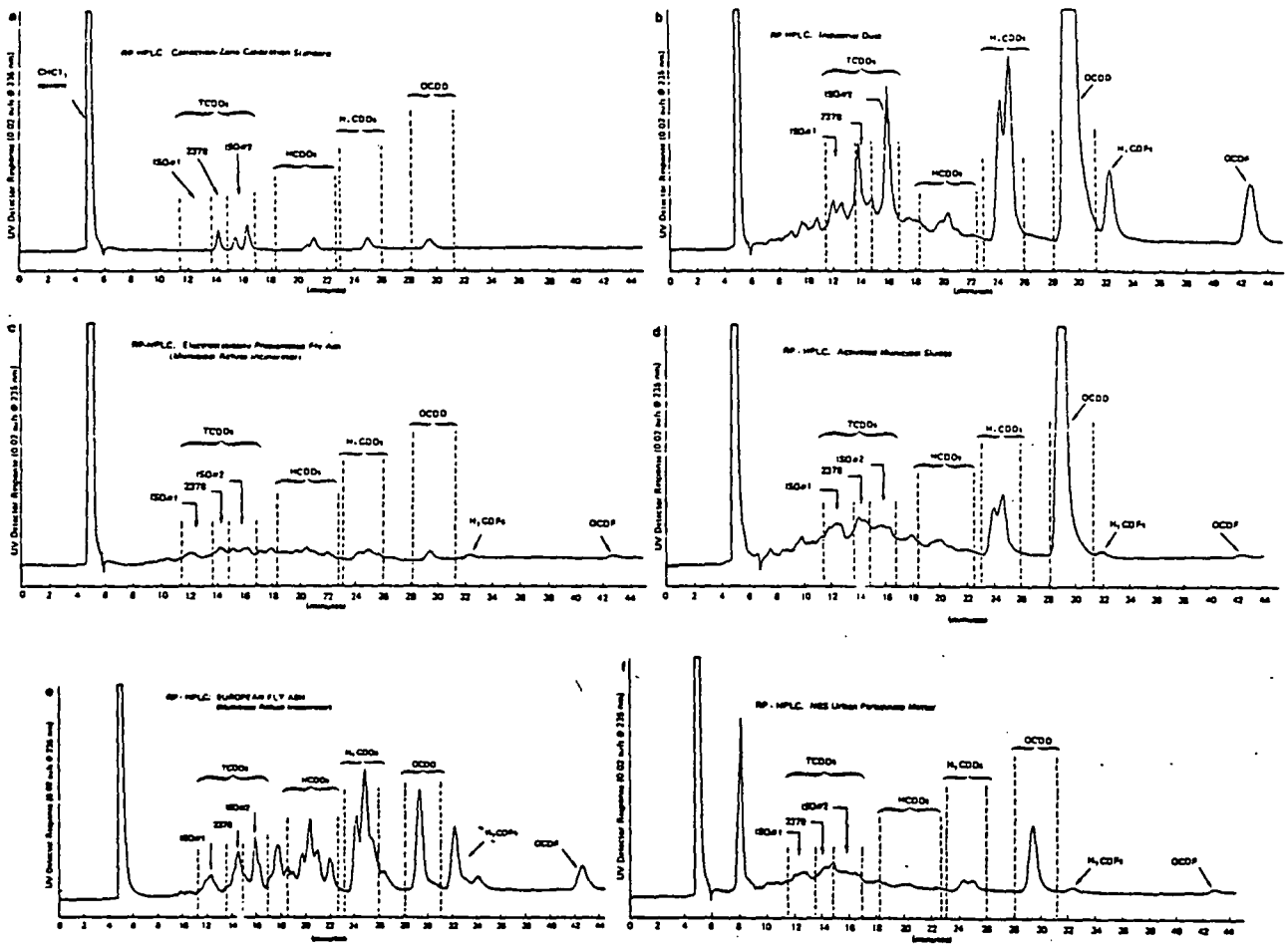


Figure 3. RP-HPLC fractionation chromatograms: (a) calibration standard, (b) industrial dust, (c) electrostatic fly ash, (d) municipal sludge, (e) European fly ash, (f) NBS urban particulates.

this information, appropriate fractions can be collected from the silica-HPLC which permit isomer-specific GC-LRMS identification and quantitation.

The silica-HPLC TCDDs fractionation scheme in Table III is designed to provide maximum isomer-specific information when using our packed-column GC-LRMS analysis, while minimizing the total number of fractions collected. Remembering that the primary goal was to provide the highest quality analytical data for 2378-TCDD, this scheme is adequate. Examination of the GC packed column relative retention times (GC rel RT, TCDD retention time relative to ^{13}C-2378-TCDD) for all TCDDs present in the RP-2378-TCDD fraction indicates that four other TCDDs have GC rel RTs within ±0.050 (~12 s for 4 min absolute retention time for ^{13}C-2378-TCDD) of 2378-TCDD. Arbitrarily defining GC rel RT ±0.050 as the minimum GC pakced column separation for qualitative identification of a TCDD isomer from 2378-TCDD and then direct GC-LRMS analysis of the RP-2378-TCDD fraction would yield a 2378-TCDD value which could include a maximum of four other TCDD isomers (2378-TCDD + 4). However, examination of the silica HPLC relative retention times (Sil rel RT, TCDD retention time relative to 2378-TCDD) for these TCDDs indicates that 2378-TCDD is the first isomer to elute. The next isomer to elute is 1237/1238-TCDD (Sil rel RT 1.10); however, even at the minimum acceptable silica-HPLC retention time for 2378-TCDD which is ~12.5 min, this isomer is separated by ~1.75 min. The remaining nine TCDD isomers, other than 2378-TCDD, present in the RP-2378-TCDD fraction can be determined as single isomers with the exception of those in Sil Fraction No. 1. Although 1237-, 1238-, 1247-, and 1248-TCDD are essentially baseline separated by silica-HPLC, attempts to collect them in individual fractions under conditions where the species cannot be observed by a UV detector would be difficult. Hence a single fraction is collected for GC-LRMS analysis. As indicated by the respective GC rel RTs, these isomers can be determined as a total for 1237- and 1238-TCDD and a total for 1247- and 1248-TCDD.

Three of the TCDD isomers present in RP-Iso No. 1 are sacrificed in order to ensure maximum recovery of 2378-TCDD in the following RP-HPLC fraction. The consequence of this situation is the possible presence of 1268/1279-TCDD (Sil rel RT 1.238), 1369-TCDD, and 1478-TCDD in the RP-2378-TCDD fraction. Regarding their effect upon the isomer-specific determination of 2378-TCDD, it can be observed that no interference occurs by virtue of both their respective silica-HPLC rel RTs and their GC-packed column rel RTs. However, under circumstances where the 1268/1279-TCDD (Sil rel RT 1.238) isomer is relatively high in concentration, it could be misidentified as 1237- and 1238-TCDD present in Sil Fraction No. 1 of the RP-2378-TCDD fraction. This interference results from similar GC rel RTs for these isomers as indicated in Table III. The 1369/1478-TCDD (Sil rel RT 1.220) will not cause any similar interference problems with those TCDDs present in RP-2378-TCDD fraction—Sil Fraction No. 1 because of its GC rel RT of 0.802. The remaining isomer, 1369/1478-TCDD (Sil rel RT 1.340), if present in high concentration may interfere with 1246/1249-TCDD (Sil rel RT 1.411) in RP-2378-TCDD fraction-Sil Fraction No. 3.

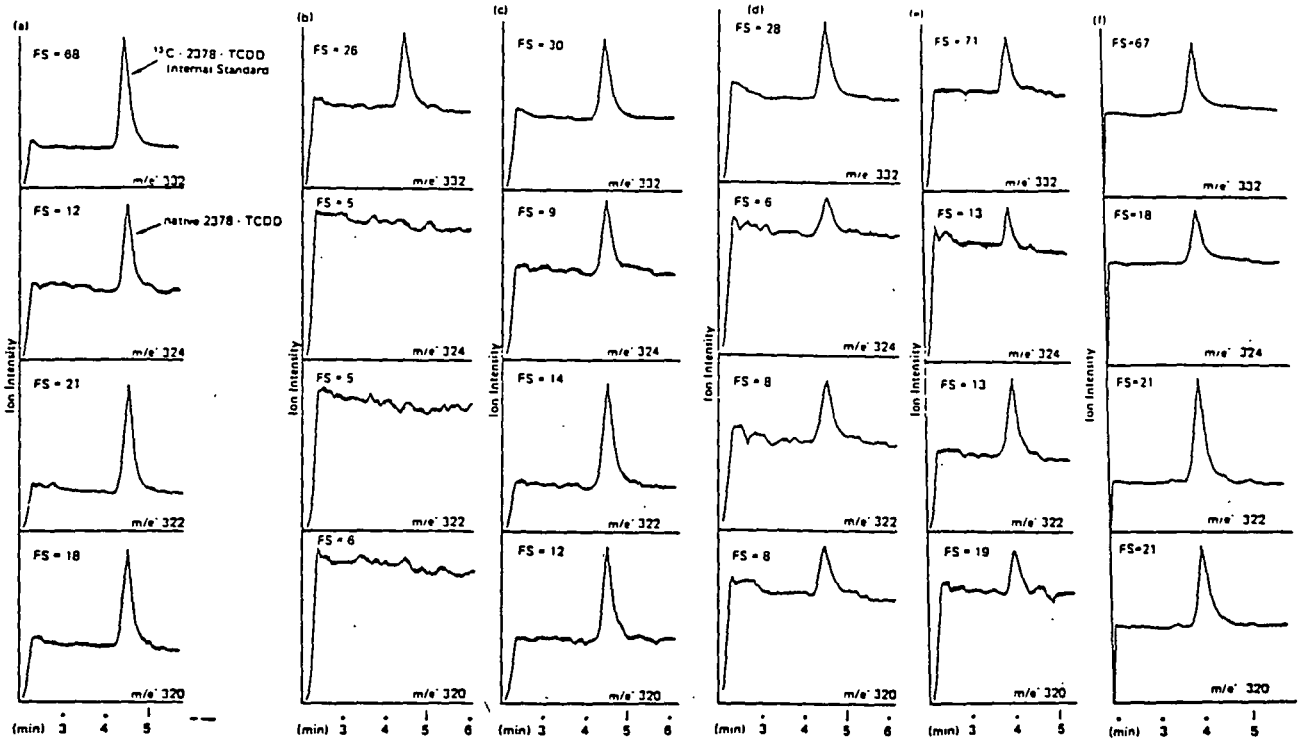


Figure 4. Isomer-specific 2378-TCDD GC-LRMS mass chromatograms: (a) calibration standard, (b) reagent blank, (c) industrial dust, (d) electrostatic fly ash, (e) municipal sludge, (f) European fly ash.

GC-LRMS mass chromatograms for the isomer-specific 2378-TCDD fractions of each particulate sample analyzed are shown in Figure 4. Native 2378-TCDD is monitored at m/e 320, 322, and 324 and ^{13}C-2378-TCDD at 332. The calibration standard (Figure 4a shown is typical for a 2-μL injection of a reference standard containing 100 pg/μL of native 2378-TCDD and 500 pg/μL of ^{13}C-2378-TCDD.

The GC-LRMS mass chromatograms in Figure 5 compare the analysis of the RP-2378-TCDD fraction from electrostatically precipitated fly ash for 2378-TCDD, before and after silica-HPLC refractionation. As a means of ensuring homogeneity, a 2-g portion of sample was processed through the cleanup including RP-HPLC fractionation. At this point the RP-2378-TCDD fraction was divided into two equal portions, each equivalent to 1 g of original sample. One portion was analyzed directly by GC-LRMS as illustrated in Figure 5a. The other portion was further fractionated by silica-HPLC, the Sil Fraction 2378 collected, and this residue analyzed by GC-LRMS (Figure 5b). Comparison of 2378-TCDD quantitation for these residues yields 1500 pptr before silica-HPLC refractionation, and 430 pptr after. The value obtained before silica-HPLC refractionation must be qualified as being the concentration of 2378-HPLC plus four possible unseparated isomers (see Table IV).

Isomer-specific TCDD analysis data for each of the described particulate samples appear in Tables IV and V. Quantitation of TCDDs was accomplished by averaging the observed response at m/e 320, 322, and 324 for all cases except where denoted. Instrumental calibration for all TCDD isomers was based upon the observed responses for a primary standard of 2378-TCDD. The listed concentrations for 2378-TCDD have been corrected for recovery of the ^{13}C-2378-TCDD internal standard as given in Table V. Concentrations given for all other TCDD isomers represent absolute observed values. The limit of detection (LoD) for all species was defined as 2.5 × peak-to-valley noise in a region nearby the expected elution time. Observed concentrations less than the LoD are listed as not detected (ND).

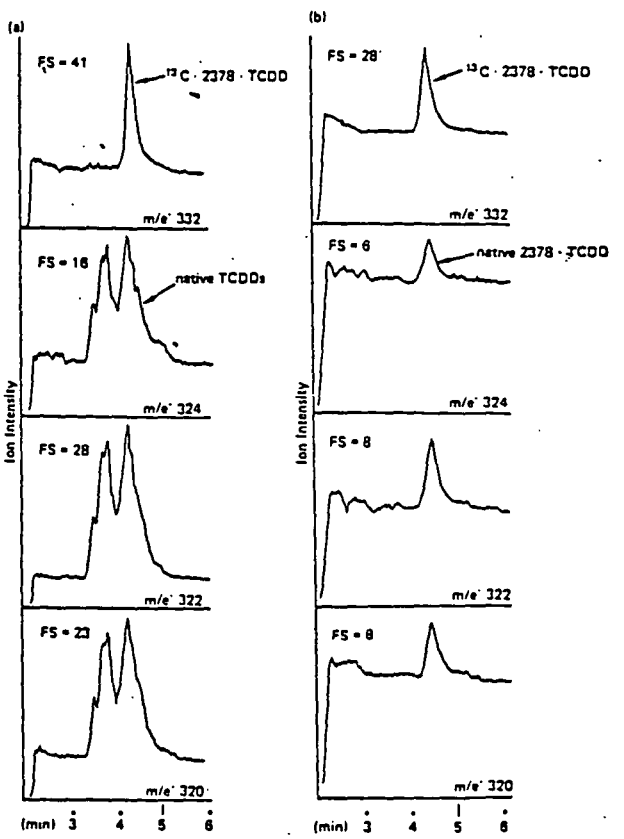


Figure 5. Comparative 2378-TCDD GC-LRMS mass chromatograms for electrostatic fly ash (a) after RP-HPLC (RP-2378 fraction) (b) after silica-HPLC (silica-2378 fraction).

As a means of investigating the degree of reliability associated with the isomer-specific determination of 2378-TCDD in a sample containing equivalent concentrations of all 21 other

Table III. TCDD Isomer Silica-HPLC Fractionation Scheme and Specific Retention Indices

TCDD isomer	silica-HPLC rel RT[a]	Sil collection zone rel RT[a]	GC packed column rel RT[b]
RP-Isol No. 1 Fraction TCDDs			
Sil fraction no. 1		1.180–1.370	
1268/1279-TCDD	1.238[c]		0.956
	1.291		1.065
1369/1478-TCDD	1.220[c]		0.802
	1.340[c]		0.907
Sil fraction no. 2		1.455–1.850	
1269-TCDD	1.702		0.998
1469-TCDD	1.497		0.912
1267/1289-TCDD	1.623		1.081
	1.795		1.200
RP-2378 Fraction TCDDs			
Sil fraction 2378		0.950–1.050	
2378-TCDD	1.000		1.006[d]
Sil fraction no. 1		1.050–1.244	
1237/1238-TCDD[e]	1.100		0.979
	1.128		0.990
1247/1248-TCDD[e]	1.154		0.854
	1.199		0.857
Sil fraction no. 2		1.244–1.300	
1278-TCDD	1.288		0.893
Sil fraction no. 3		1.300–1.385	
1246/1249-TCDD	1.328		0.896
1236/1239-TCDD	1.356		1.037
	1.350		0.969
Sil fraction no. 4		1.385–1.450	
1246/1249-TCDD	1.411		0.898
RP-Iso No. 2 Fraction TCDDs			
Sil fraction no. 1[f]		0.900–1.050	
1368-TCDD	0.940		0.729
1379-TCDD	0.977		0.771
1378-TCDD	1.000		0.858
Sil fraction no. 2[f]		1.210–1.288	
1234-TCDD	1.248		0.960

[a] Silica-HPLC rel RT = retention time relative to 2378-TCDD (±0.010). [b] GC packed column rel RT = retention time relative to ^{13}C-2378-TCDD (±0.005). [c] See text for recovery information. [d] Native 2378-TCDD elutes slightly later than ^{13}C-2378-TCDD. [e] Related isomers typically reported as a total. [f] Fractions typically combined prior to GC-LRMS analysis.

TCDD isomers, we intentionally fortified a second portion of muncipal sludge with each TCDD isomer at the levels shown in Table VI. Neither 1237- or 1238-TCDD was added due to their natural presence at 230 pptr (see Table V). Analysis of the fortified sample yielded the recovery data shown in Table VI. Regarding the 2378-TCDD data, the amount found was corrected for the recovery of the ^{13}C-2378-TCDD and also for the 20 pptr natural 2378-TCDD previously observed in the sample. These data indicate that no other TCDD isomer interferes with the determination of 2378-TCDD when this analytical procedure is used. Recovery values given for all other TCDD isomers represent absolute observed values and were corrected for natural levels when necessary as listed in Table VI.

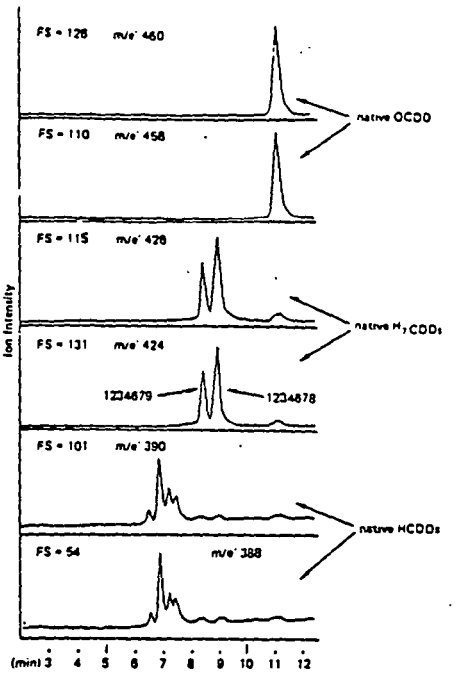


Figure 6. Higher chlorinated dioxin GC-LRMS mass chromatograms for electrostatic fly ash.

Typical temperature programmed GC-LRMS mass chromatograms for the determination of higher chlorinated dioxins appear in Figure 6. For the analysis of electrostatically precipitated fly ash the RP-HPLC HCDDs, H_7CDDs, and OCDD fractions were combined prior to GC-LRMS examination (see Figure 3c). As a means of overcoming problems associated with samples having relatively large amounts of native chlorinated dioxins compared to the 1–20 ng of fortified internal standards, a complete method validation study was conducted for HCDDs, H_7CDDs, and OCDD ranging from 50 pptr to 10 ppm (μg/g) and from 10 pptr to 5 ppb for 2378-TCDD. The control particulate sample used was a sandy loam soil, to which was added ~150 μL of Mobile 1 synthetic engine lubricant per 20 g, as a means of increasing the total organics content to better simulate typical particulates. The following native CDD standards were used for sample fortification: 2378-TCDD, 123678-HCDD, 123679/123689-HCDD (Sil rel RT 1.039), 1234678-H_7CDD, and OCDD. The results of this

Table IV. Chlorinated Dioxins Observed in Environmental Particulate Samples

		parts per billion				
CDDs	reagent blank, ng	industrial dust	electrostatic flyash	municipal sludge	European flyash	NBS urban particulates
2378-TCDD + 4 isomers[a]	ND (0.06)	...[b]	1.5[b]	...[b]	...[b]	0.12 (0.12)[e]
other TCDDs (17 isomers)	ND (0.04)	...[b]	...[b]	...[b]	...[b]	0.16 (0.08)
HCDDs[c] (10 isomers)	ND (0.18)	ND (14)	14	2.1	550[d]	2 (2)
1234679-H_7CDD[c]	ND (0.14)	200	11	14	470	16
1234678-H_7CDD[c]	ND (0.14)	220	17	15	570	18
OCDD[c]	ND (0.29)	4000	30	180	650	210

[a] RP-HPLC RP-2378 fraction analyzed directly by GC-LRMS and not isomer specific as described in text. [b] Sample fully fractionated for isomer-specific results given in Table V. [c] Observed values without correction run as part of validation work reported in Table VII. [d] For "semi" isomer specific see Table VIII. [e] ^{13}C-2378-TCDD recovery 78% and value listed has been corrected, see Table V for others, and ND = compound not detected at limit of detection in parentheses and no parentheses indicates detected signal > 10× limit of detection.

Table V. Isomer-Specific TCDD Analyses of Environmental Particulate Samples

TCDD isomer	reagent blank, pg	parts per trillion: industrial dust	electrostatic flyash	municipal sludge	European flyash
2378-TCDD[a]	ND (40)	1100	430 (110)	20 (2)	2300
1269-TCDD	ND (20)	ND (40)	190 (60)	ND (2)	1000 (140)
1469-TCDD	ND (20)	ND (50)	ND (50)	ND (2)	250 (140)
1267/1289-TCDD Sil rel RT 1.623	ND (20)	ND (50)	100 (60)	ND (2)	300 (140)
1267/1289-TCDD Sil rel RT 1.795	ND (20)	ND (50)	120 (60)	ND (2)	500 (140)
1268/1279-TCDD Sil rel RT 1.238	ND (30)	...[b]	190 (90)[c]	...	1000[c]
1268/1279-TCDD Sil rel RT 1.291	ND (30)	ND (50)	310 (90)	3 (3)[d]	1500
1369/1478-TCDD Sil rel RT 1.220	...	...	...	...	...
1369/1478-TCDD Sil rel RT 1.340	...	...	...	...	...
1278-TCDD	ND (60)	ND (40)	ND (80)	ND (3)	3100
1236/1239-TCDD Sil rel RT 1.356	ND (60)	ND (60)	280 (110)	ND (3)	1500
1236/1239-TCDD Sil rel RT 1.350	ND (60)	ND (60)	150 (110)	ND (3)	800 (400)
1237/1238-TCDD Sil rel RT 1.100 1237/1238-TCDD Sil rel RT 1.128	ND (60)	240 (50)[e]	720[e]	230[e]	8500[e]
1246/1249-TCDD Sil rel RT 1.328 1246/1249-TCDD Sil rel RT 1.411	ND (60)	ND (60)[e]	730 (110)[e]	ND (3)[e]	2000[e] 1500
1247/1248-TCDD Sil rel RT 1.154 1247/1248-TCDD Sil rel RT 1.199	ND (60)	140 (50)	310 (70)	8 (2)	6900
1378-TCDD	ND (20)	560 (110)	1370 (150)	23 (5)	13200
1379-TCDD	ND (20)	1340	1160 (150)	13 (5)	7000
1368-TCDD	ND (20)	2780	1320 (150)	13 (5)	16200
1234-TCDD	ND (20)	180	370 (150)	ND (30)	2100
total TCDDs	ND	6340	7750	310	69800
^{13}C-2378-TCDD % recovery	63%	59%	54%	61%	56%

[a] Corrected for ^{13}C-2378-TCDD recovery and all other isomers are absolute observed. [b] ... = not recovered as described in text. [c] Observed but recovery questionable. [d] Detected on *m/e* 322 only. [e] Possible isomer interference as described in text.

Table VI. Isomer-Specific TCDD Analysis of Municipal Sludge after Fortification

TCDD isomer	concn in pptr: added	found	% recovery
2378-TCDD	143	140	98[a]
1269-TCDD	150	108	72
1469-TCDD	166	122	73
1267/1289-TCDD Sil rel RT 1.623	150	126	84
1267/1289-TCDD Sil rel RT 1.795	171	145	85
1268/1279-TCDD Sil rel RT 1.238	137	...[b]	...
1268/1279-TCDD Sil rel RT 1.291	140	69	49
1369/1478-TCDD Sil rel RT 1.220	143	...	...
1369/1478-TCDD Sil rel RT 1.340	151	...	...
1278-TCDD	160	104	65
1236/1239-TCDD Sil rel RT 1.356	147	103	70
1236/1239-TCDD Sil rel RT 1.350	146	80	55
1237/1238-TCDD Sil rel RT 1.100 1237/1238-TCDD Sil rel RT 1.128	[c]	(180)[d]	
1246/1249-TCDD Sil rel RT 1.328 1246/1249-TCDD Sil rel RT 1.411	141 151	220[e]	75
1247/1248-TCDD Sil rel RT 1.154 1247/1248-TCDD Sil rel RT 1.199	131 163	203[e]	69
1378-TCDD	171	151	88
1379-TCDD	171	138	81
1368-TCDD	101	45	45
1234-TCDD	143	122	85

[a] Corrected for recovery of ^{13}C-2378-TCDD (72%) and native 2378-TCDD present given in Table V, all other isomers are absolute observed. [b] ... = not recovered as described in text. [c] Total not added. High native concentration given in Table V. [d] Absolute amount observed in this sample. [e] Total.

study appear in Table VII. These data indicate that the average recoveries of HCDDs, H_7CDDS, and OCDD over the described concentrations range are reasonably constant and are between 70 and 80%. Because typical particulate samples contain higher chlorinated CDDs within this range, recovery factors derived from the validation can be used. Since ^{13}C-labeled internal standards are added to all samples, whenever very low native concentrations are observed appropriate correction factors can be applied. Note that recovery values reported for TCDD have been corrected for the observed ^{13}C-2378-TCDD internal standard recoveries after RP-HPLC fractionation.

Table VII. Chlorinated Dioxin Recovery and Precision Data for Fortified Sandy Loam Soil[a]

	2378-TCDD[b]			HCDD			H$_7$CDD			OCDD		
sample no.	added, pptr	found, pptr	%	added, pptr	found, pptr	%	added, pptr	found, pptr	%	added, pptr	found, pptr	%
1	10	13	130	50	30	60	50	46	92	200	160	80
2	20	28	140	100	72	72	100	75	75	400	330	83
3	20	21	105	100	57	57	100	65	65	400	260	65
4	50	49	98	250	160	64	250	170	68	1000	730	73
5	50	45	90	250	180	72	250	200	80	1000	820	82
6	50	51	102	250	170	68	250	200	80	1000	780	78
7	50	53	106	250	170	68	250	170	68	1000	720	72
8	50	50	100	250	190	76	250	210	84	1000	880	88
9	50	50	100	250	160	64	250	160	64	1000	700	70
10	50	47	94	250	180	72	250	180	72	1000	690	69
11	50	52	104	250	170	68	250	160	64	1000	690	69
12	100	97	97	500	410	82	500	430	86	2000	1900	95
13	100	109	109	500	440	88	500	460	92	2000	2060	103
14	5000	5350	107	1×10^3	8.1×10^3	87	5×10^3	4.5×10^3	90	10×10^3	8.4×10^3	84
15	5000	5400	108	1×10^3	9.1×10^3	91	5×10^3	4.7×10^3	94	10×10^3	9.0×10^3	90
$\bar{x}$ all[c]			106			73			78			80
σ all[c]			13			10			11			11
$\bar{x}$ prec[d]	50	49.6	99.2	250	173	69	250	181	72	1000	751	75
σ prec[d]		2.6	5.2		10.4	6.0		19.6	10.8		69.4	9.2

[a] Data for all species obtained by GC-LRMS analysis of appropriate RP-HPLC fractions. 2378-TCDD values corrected for ^{13}C-2378-TCDD internal standard recovery, other CDDs are absolute observed. [b] Corrected for ^{13}C-2378-TCDD where average recovery was 59.8% for all samples. [c] $\bar{x}$ all and σ all represent the mean and standard deviation of all samples. [d] $\bar{x}$ prec and σ prec represent the mean and standard deviation of samples 4–11 to determine precision of the analysis.

Table VIII. "Semi" Isomer-Specific HCDD Analysis Data for European Flyash, Absolute Values Reported

HCDD isomer[a]	parts per billion: reagent blank	European flyash
124679/124689-HCDD Sil rel RT 0.958 124679/124689-HCDD Sil rel RT 0.972	ND (0.13)[b,c]	82[c]
123468-HCDD	ND (0.13)	9 (9)
123679/123689-HCDD Sil rel RT 0.970 123679/123689-HCDD Sil rel RT 1.039 123469-HCDD	ND (0.13)[c]	260[c]
123478-HCDD 123678/123789-HCDD Sil rel RT 0.974	ND (0.13)[c]	110[c]
123678/123789-HCDD Sil rel RT 1.060 123467-HCDD	ND (0.13)[c]	85 (9)[c]

[a] HCDD Sil rel RT = retention time relative to 2378-TCDD by silica-HPLC (Table II). [b] ND (0.13) is not detected with limit of detection in ppb based on flyash sample size. [c] Total.

GC-LRMS analysis data for higher chlorinated CDDs appear in Tables IV and VIII. Table VIII illustrates a format for HCDD determination that is "semi"-isomer specific. In this case, the total RP-HCDDs fraction was analyzed directly by packed-column GC-LRMS. However, because GC rel RTs have been experimentally determined (see Table II) for all 10 individual HCDD isomers, we can separate the HCDDs observed into five distinct groups. Within each group only a limited number of isomers are possible. These analyses are accomplished by using isothermal column condition (~270 °C) so as to maximize the separation power of the column and to improve relative retention time measurements.

CONCLUSIONS

Although this paper demonstrates the applicability of a multiple-step procedure to isomer-specifically determine a variety of CDDs in environmental particulate samples, we have also applied the technique to many other matrices successfully. Simple modification of the preliminary matrix extraction has permitted the analysis of tissues, human milk, vegetable matter, chemical products, and wastes without sacrificing high sensitivity or isomer specificity. This procedure, utilizing packed-column GC-LRMS, has provided reliable results for several heavily contaminated matrices where the combination of a less sophisticated cleanup followed by both packed and capillary column GC-HR MS has failed. Interested individuals may request a more thorough discussion of the method development experiments from the authors.

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Secondary Ion Mass Spectra of Diquaternary Ammonium Salts

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Molecular dications emitted by momentum transfer processes are observed in secondary ion mass spectra (SIMS) of diquaternary ammonium salts. The relationship between molecular structure and the observation of dications is explored. Large intercharge separations, corresponding to lessened intramolecular coulombic repulsions, are observed to correlate with dication detection. Fragmentation with charge separation is facilitated by small intercharge distances and can preclude observation of the dication. Electron attachment to yield the monocation is an alternative to dication emission when the structure of the dication facilitates reduction. This occurs, for example, for the herbicide diquat (*N,N′*-ethylene-2,2′-bipyridyl dibromide) which is detected as its monocation. Complete spectra of diquaternaries can be taken with nanogram size samples.

Secondary ion mass spectrometry (SIMS) has recently been shown to be a sensitive method for the characterization of organic salts (*1–4*). Reported here is the observation of intact organic dications emitted from diquaternary ammonium salts upon sputtering. This constitutes the first observation of multiply charged organic molecular ions in SIMS. The result is of interest with regard to both analytical applications of SIMS and the fundamentals of ionization during sputtering. Specifically, some biologically important compounds, such as the herbicides paraquat and diquat and the curare alkaloids, have the diquaternary structure, so that SIMS may facilitate their characterization. In addition, studies on organic dications reflect the degree to which electron attachment occurs during sputtering. This process yields observable charged products for dications, but neutrals are sputtered when monocations are reduced during ion bombardment.

EXPERIMENTAL SECTION

All compounds were synthesized by using standard methods for the preparation of quaternary ammonium salts. The organic salts were burnished onto a 1 cm^2 roughened foil of either silver or platinum prior to SIMS analysis using argon primary ions at 5 keV and 0.3–0.5 nA primary ion current. Beam diameter was approximately 1 mm and pressures in the ultra-high-vacuum chamber remained below 1×10^{-6} torr during the course of the experiments.

All spectra were taken with Riber SIMS system using a quadrupole mass analyzer, Channeltron electron multiplier, and pulse-counting electronics.

Intercharge distances were measured by using Dreiding models; charge localization on nitrogen was assumed and the maximum distance in the unstrained molecule is reported. Intercharge distances (r) were used to calculate coulombic repulsive energies (T) from T (eV) = 14.6/r (Å).

RESULTS AND DISCUSSION

The SIMS spectrum of *N,N′*-bis(dimethyl)-4,4′-trimethylenedipiperidine diiodide (1) is shown in Figure 1. This spectrum provides both the molecular weight (inferred from the highest mass doubly charged ion, 268^{2+}) and structural information on the compound. Emission of the doubly charged species is confirmed by the observation of the ^{13}C isotope peak one-half mass unit above the dication peak (m/z 134.5 in Figure 2). Changing the counterion does not affect the SIMS spectrum; for example, the dibromide and diiodide of compound 1 gave identical SIMS spectra.

Analogous results were obtained for *N,N′*-bis(ethylmethyl)-4,4′-trimethylenedipiperidine diiodide (2) and for the aromatic compounds *N,N′*-bis(trimethyl)-4,4′-methylenedianiline diiodide (3) and *N,N′*-bis(dimethylethyl)-4,4′-methylenedianiline diiodide (4). The spectrum of compound 3 is shown in Figure 3; the dication, 284^{2+} at m/z 142 is of relatively low abundance, but its ^{13}C isotope is well resolved in high-resolution scans.

A considerable number of diquaternary salts (5–19, Table I) did not exhibit observable dications. Compounds 18 and 19, while they did not yield molecular dications, did show the corresponding singly charged ions in their SIMS spectra. Compounds 5–17 may fail to exhibit dications because they fragment by a favorable charge separation route, $M^{2+} \rightarrow M_1^+ + M_2^+$. This is indicated by the absence of both singly and doubly charged molecular ions for these samples.

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temperature of the water bath to 85 to 90°C. Concentrate the extract as in section 11.2.6 except use hexane to prewet the column. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane.

11.2.8 Add a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 1 mL of hexane to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches about 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 mL hexane. Proceed to section 11.3.2. If further processing is to be delayed, the extract should be quantitatively transfered to a Teflon sealed screw-cap vial and store refrigerated and protected from light.

11.2.9 Fill the sample bottle with water to the mark and measure the volume to the nearest 10 mL in a 1 L graduated cylinder.

11.3 Column Chromatograph

11.3.1 Column Preparation

11.3.1.1 Column 1: Place 1.0 g of silica gel into a 1 cm x 20 cm column and tap the column gently to settle the silica gel. Add 2 g sodium hydroxide-impregnated silica gel, 1 g silica gel, 4.0 g of sulfuric acid-impregnated silica gel, and 2 g silica gel. Tap column gently after each addition.

11.3.1.2 Column 2: Place 6.0 g of alumina into a 1 cm x 30 cm column and tap the column gently to settle the alumina. Add a 1-cm layer of purified sodium sulfate to the top of the alumina.

11.3.1.3 Add hexane to each column until the packing is free of channels and air bubbles. A small positive pressure (5 psi) of clean nitrogen can be used if needed.

11.3.2 Quantitatively transfer the hexane sample extract from the concentrator tube to the top of the silica gel in Column 1. Rinse the concentrator tube with two 0.5 mL portions of hexane; transfer rinses to Column 1.

11.3.3 With 90 mL of hexane, elute the extract from Column 1 directly into Column 2 containing alumina and sodium sulfate.

11.3.4 Add 20 mL of hexane to Column 2 and elute until the hexane level is just below the top of the sodium sulfate; discard the eluted hexane.

11.3.5 Add 20 mL of 20% methylene chloride/80% hexane (volume/volume) to Column 2 and collect the eluate.

11.3.6 Reduce the volume of the eluate with a gentle stream of filtered dry nitrogen. When the volume of the eluate is about 1 to 2 mL, transfer the eluate to the Carbopack column (Section 11.4.4). Rinse the eluate container with two 0.5 mL portions of hexane; transfer the rinses to the Carbopack column. CAUTION: Do not evaporate the sample extract to dryness. NOTE: The carbopack cleanup is not required for water samples unless needed to meet detection sensitivity criteria.

11.4 Carbopack Column Chromatography Procedure

11.4.1 Thoroughly mix 3.6 g of Carbopack C (or equivalent) with 16.4 g of Celite 545 (or equivalent) in a 40 mL vial and activate by heating in an oven at 130°C for 6 hours. Store in a desiccator. CAUTION: Check each new batch of mixed Carbopack/Celite to ensure TCDD recovery of >50%. Subject the low level concentration calibration solution to this procedure and measure the quantity of labeled and unlabeled 2,3,7,8-TCDD.

11.4.2 Insert a small plug of glass wool into a disposable pipet approximately 15 cm long by 7 mm O.D. Apply suction with a vacuum aspirator attached to the pointed end of the pipet, and add the Carbopack/Celite mixture until a 2 cm packing is obtained.

11.4.3 Pre-elute the column with:

11.4.3.1 2 mL toluene

11.4.3.2 1 mL of mixture of 75% (by volume) methylene chloride, 20% methanol and 5% benzene

11.4.3.3 1 mL of 50% (by volume) cyclohexane and 50% methylene chloride

11.4.3.4 2 mL of hexane

11.4.4 While the column is still wet with hexane add the sample extract from section 11.2.6. Elute the column with the following sequence of solvents and discard the eluates.

11.4.4.1 2 mL hexane

11.4.4.2 1 mL of 50% (by volume) cyclohexane and 50% methylene chloride

11.4.4.3 1 mL of 75% (by volume) methylene chloride, 20% methanol and 5% benzene

11.4.5 Elute with 2 mL of toluene and collect the elutate, which contains the TCDD. Transfer the rinses to a 1-mL amber mini-vial with conical reservoir with further concentration as necessary. CAUTION: Do not evaporate the sample extract to dryness.

11.3.6 Store the sample extract in the dark at 4°C until just before GC/MS analysis.

11.5 GC/MS Analysis

11.5.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature. With a stream of dry, filtered nitrogen, reduce the extract/blank volume to near dryness. Immediately before GC/MS analysis, add 5 uL of the 10 ng/uL recovery standard solution and adjust the extract or blank volume to 50 uL with isooctane.

11.5.2 Inject a 2-uL aliquot of the extract into the GC, operated under conditions previously used (Section 9) to produce acceptable results with the performance check solution.

11.5.3 Acquire mass spectral data for the following selected characteristic ions: m/z 259, 320, and 322 for unlabeled 2,3,7,8-TCDD; m/z 328 for $^{37}Cl_4$-2,3,7,8-TCDD; and m/z 332 and 334 for $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-1,2,3,4-TCDD. Use the same data acquisition time and MS operating conditions previously used (Section 9.2.6) to determine response factors.

11.6 Identification Criteria. NOTE: Refer to Exhibit E, Section 7, for application of identification criteria.

11.6.1 Retention time (at maximum peak height) of the sample component must be within 3 seconds of the retention time of the $^{13}C_{12}$-2,3,7,8-TCDD. Retention times are required for all chromatograms, but scan numbers are optional. These parameters should be printed next to the appropriate peak.

11.6.2 The integrated ion currents detected for m/z 259, 320, and 322 must maximize simultaneously. If there are peaks that will affect the maximization or quantitation of peaks of interest, attempts should be made to narrow the scan window to eliminate the interfering peaks. This should be reported on a separate chromatogram.

11.6.3 The integrated ion current for each analyte and surrogate compound ion (m/z 259, 320, 322 and 328) must be at least 2.5 times background noise and must not have saturated the detector; internal standard ions (m/z 332 and 334) must be at least 10 times background noise and must not have saturated the detector.

11.6.4 Abundance of integrated ion counts detected for m/z 320 must be $\geq$67% and $\leq$90% of integrated ion counts detected for m/z 322.

11.6.5 Abundance of integrated ion counts detected for m/z 332 must be $\geq$67% and $\leq$90% of integrated ion counts detected for m/z 334.

11.6.6 The recovery of the internal standard $^{13}C_{12}$-2,3,7,8-TCDD should be within a 40 percent to 120 percent recovery window. This is an advisory limit only, an action window may be set when sufficient data is available.

12. CALCULATIONS

12.1 Concentration

12.1.1 Calculate the concentration of 2,3,7,8-TCDD using the formula:

$$C_x = \frac{A_x \cdot Q_{is}}{A_{is} \cdot RF_n \cdot W}$$

where C_x = 2,3,7,8-TCDD concentration in ug/kg or ug/L

A_x = the sum of integrated ion abundance detected for m/z 320 and 322

A_{is} = the sum of integrated ion abundances detected for m/z 332 and 334 (characteristic ions of $^{13}C_{12}$-2,3,7,8-TCDD, the internal standard)

Q_{is} = quantity (in ng) of $^{13}C_{12}$-2,3,7,8-TCDD added to the sample before extraction

RRF_n = calculated mean response factor for unlabeled 2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD

W = weight (in g) of wet soil or sediment sample or volume of water extracted (in mL).

12.1.2 If the calculated concentration of unlabeled 2,3,7,8-TCDD exceeds 100 ug/kg for soil/sediment or 1 ug/L for water, which is the maximum concentration of the concentration calibration solutions, the linear range may have been exceeded, and a smaller aliquot of that sample must be analyzed. Accurately weigh to three significant figures a 1-g aliquot of the wet soil/sediment or measure a 100 mL aliquot of water. Add the 1.5 mL acetone dilution of 100 uL of the sample fortification solution (Section 7.8), just as for the larger sample aliquot. Extract and analyze.

12.1.3 Calculate the concentration of the internal standard $^{13}C_{12}$-2,3,7,8-TCDD using the formula:

$$C_{is} = \frac{A_{is} \cdot Q_{rs}}{A_{rs} \cdot RF_i \cdot W}$$

where

C_{is} = concentration of $^{13}C_{12}$-2,3,7,8-TCDD in ug/kg or ug/L

A_{is} = sum of integrated ion abundances for m/z 332 and 334 for $^{13}C_{12}$-2,3,7,8-TCDD

A_{rs} = sum of integrated ion abundances for m/z 332 and 334 for $^{13}C_{12}$-1,2,3,4-TCDD

Q_{rs} = quantity (in ng) of $^{13}C_{12}$-1,2,3,4-TCDD added to the sample before injection

RF_i = calculated mean response factor for $^{13}C_{12}$-1,2,3,4-TCDD

W = weight (in g) of wet soil or sediment sample or volume of water extracted (in mL).

12.2 Estimated Maximum Possible Concentration — For samples in which no unlabeled 2,3,7,8-TCDD was detected, calculate the estimated maximum possible concentration, which is the concentration required to produce a signal with peak height of 2.5 times the background signal level. The background level is determined by measuring the range of the noise (minimum to maximum) for either m/z 320 or 322 in the appropriate region of the SICP (as defined in section 13.11), multiplying that noise height by 2.5, and relating the product height to an estimated concentration that would produce that product height.

Use the formula:

$$MPC = \frac{2.5 \cdot A_x \cdot Q_{is}}{A_{is} \cdot RF_n \cdot W}$$

where MPC = estimated maximum possible concentration of unlabeled 2,3,7,8-TCDD required to produce A_x in ug/kg or ug/L

A_x = peak height for either m/z 320 or 322 within + 5 scans of the internal standard peak used to measure A_{is}

A_{is} = peak height of the appropriate ion characteristic of the internal standard, m/z 332 when m/z 320 is used to determine A_x, and m/z 334 when m/z 322 is used to determine A_x

Q_{is}, RF and W retain the definitions previously stated in Section 12.1.1

12.4 The relative percent difference (RPD) is calculated as follows: (See Section 5.1.1, Exhibit E.)

$$RPD = \frac{|S_1 - S_2| \times 100}{\text{Mean Concentration}} = \frac{|S_1 \quad S_2| \times 100}{\frac{S_1 + S_2}{2}}$$

S_1 and S_2 represent sample and duplicate sample results.

12.6 Percent Recovery of 2,3,7,8-TCDD in spiked field blanks =

$$\frac{\text{concentration found}}{\text{concentration added}} \times 100$$

12.7 Percent Recovery of internal standard, $^{13}C_{12}$-2,3,7,8-TCDD =

$$\frac{\text{concentration found}}{\text{concentration added}} \times 100$$

12.8 Standard deviation = $S = \sqrt{\sum_{i=1}^{N} \frac{(X_i - \bar{X})^2}{N - 1}}$

12.9 Percent relative standard deviation =

$$\frac{\text{Standard Deviation}}{\text{Mean}} \times 100 = \frac{S}{\bar{X}} \times 100$$

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APPENDIX III

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.

$$\frac{\text{gm of sample} - \text{gm of dry sample}}{\text{gm of sample}} \times 100 = \% \text{ moisture}$$

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APPENDIX IV

Tetra-Octa CDD/CDF Scan Quantitation Protocol and Analytical Standards

- Mimimal Requirements for Bidders

Analytical Standards

- 2378 TCDD, $^{13}C_{12}$, $^{37}Cl_4$
- 2378 TCDF
- Mixture of TCDD isomers to verify column resolution *
- OCDD, $^{13}C_{12}$-OCDD
- Mix of Penta CDD/CDF, Hexa CDD/CDF, Hepta CDD/CDF to establish RT windows for spiking. Continuing calibrations must be within RT windows established.

Quantitation

Quantitate TCDD, TCDF, Penta CDD, Penta CDF, Hexa CDD, Hexa CDF against $^{13}C_{12}$-2378-TCDD

(Quantitate TCDF, Penta CDF, and Hexa CDF against $^{13}C_{12}$-TCDF, ~~if available.~~)

Quantitate Hepta CDD, Hepta CDF, OCDD, OCDF against $^{13}C_{12}$-OCDD

Qualify data as "estimated" concentrations with tentative identifications unless you have access to pure isomer standards (i.e., all 38 TCDF isomers, etc.)

* Column resolution should meet Dioxin IFB ~~WA84-A002~~ WA-86M357 criteria i.e. 25% valley or lower between 2,3,7,8-TCDD and it's nearest neighbor in SIC display (Appendix VII).

APPENDIX V

DELIVERABLES REQUIRED FOR GC/MS DIOXIN/FURAN ANALYSIS

A. SAMPLE PREPARATION AND METHOD DOCUMENTATION

(1) "Cookbook" style step-by-step method including instrument/conditions, type and source of reagents.

(2) Analyst bench records describing dilutions, weighings and any unusual occurrences during prep, extraction or clean up.

(3) Calculations and method used in determination of percent lipids and percent solids (where applicable).

B. DIOXIN/FURAN QUANTITATION AND IDENTIFICATION DOCUMENTATION

(1) Detailed explanation of the quantitation and identification procedure used for all isomer classes and specific isomers.

(2) List of criteria for positive identification of 2,3,7,8-TCDD and 2,3,7,8-TCDF.

(3) Example calculations of response ratios, sample results and detection limits.

(4) Simultaneous display/offset SICs and peak areas of native, $^{13}C_{12}$- and $^{37}Cl_4$-2,3,7,8-TCDD in all samples and QC, including blanks.

(5) Simultaneous display/offset SICs and peak areas of ions monitored for each PCDD/PCDF class.

(7) List of exact ion masses for each isomer/class, current and historical response factors and retention times for positive ID.

(8) Simultaneous display/offset SICs to check for polychlorinated diphenylethers which may co-elute with the furans.

(9) Simultaneous display/offset SICs of M/Z 257, 259 in samples with positive 2, 3, 7, 8-TCDD content.

(10) Simultaneous display/offset SICs and peak areas of ions monitored, for all standards used, for each PCDD/PCDF class. Include a listing of response ratios, ion ratios and amount of each standard used.

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(11) Chronological List (date/time) of ALL standards, native spikes, method blanks, duplicates, samples, reanalyses etc.

(12) Completed copy (including sample condition of SAS packing list.

APPENDIX VI

CASE #. _____

PCDD/PCDF Concentration (PPT) as Dry Weight

ISOMER OR HOMOLOG	DATE: / Samp.#	ALIQUOT WT. (g)	DATE: / Samp.#	ALIQUOT WT. (g)	PRECISION AS RPD	PRECISION LIMITS	COMMENTS
2,3,7,8-TCDF							
^{37}Cl-2,3,7,8-TCDF % Recovery							
ng ^{37}Cl-2,3,7,8-TCDF Added							
Total TCDFs							
Total Penta CDFs							
Total Hexa CDFs							
Total Hepta CDFs							
OCDF							
- - - - - - - - - -	- - - - - - - - - -		- - - - - - - - - -		- - - - - - - - - -	- - - - - - - - - -	- - - - - - - - - -
2,3,7,8-TCDD							
^{37}Cl-2,3,7,8-TCDD % Recovery							
ng ^{37}Cl-2,3,7,8-TCDD Added							
Total Tetra CDDs							
Total Penta CDDs							
124679 & 124689 H_6CDD							
123679 & 123689 H_6CDD							
123469 H_6CDD							
123478 H_6CDD							
123678 H_6CDD							
123467 & 123789 H_6CDD							
Total H_6CDDs							
^{37}Cl-123478 H_7CDD % Recovery							
ng ^{37}Cl-1232478 H_7CDD Added							
1234679 H_7CDD							
1234678 H_7CDD							
TOTAL H_7CDD							
OCDD							
^{37}Cl-OCDD %Recovery							
ng ^{37}Cl-OCDD Added							

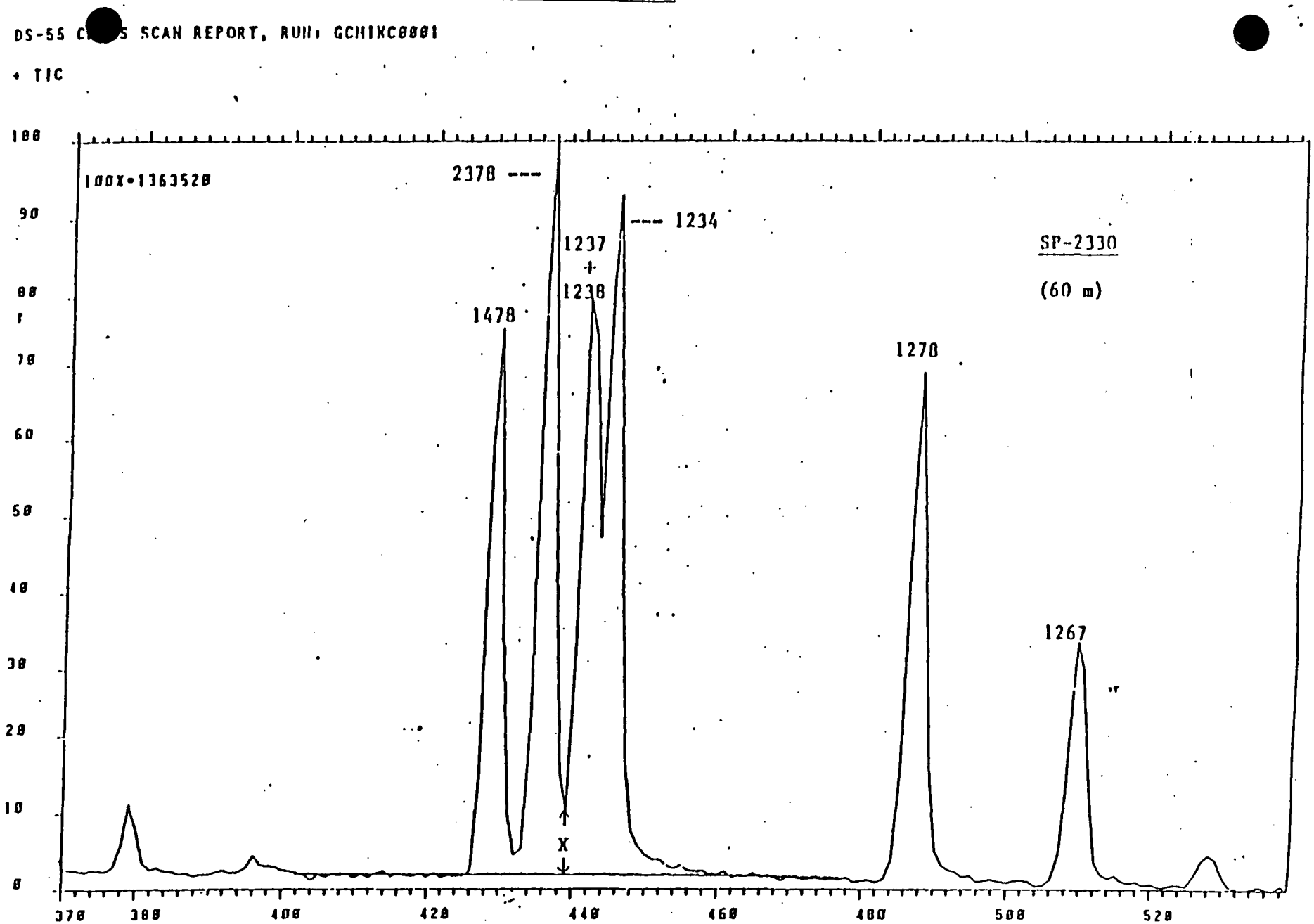

Figure 2. Selected ion current profile for m/z 320 and 322 produced by MS analysis of performance check solution using a 60-m SP-2330 fused silica capillary column and conditions listed in Table I.

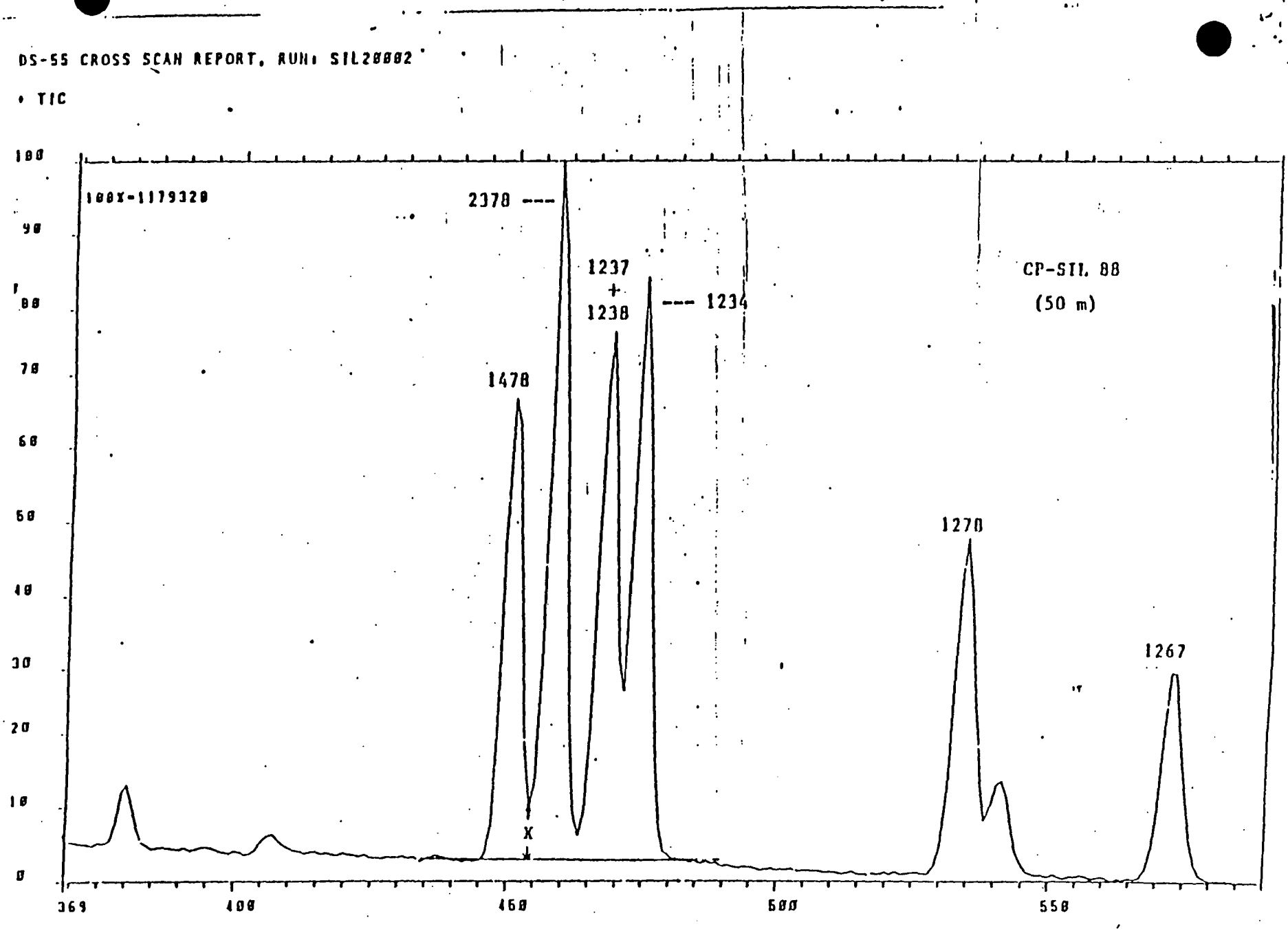

Figure 3. Selected ion current profile for m/z 320 and 322 produced by MS analysis of performance check solution using a 50-m CP-SIL 88 fused silica capillary column and conditions listed in Table 1.

Appendix D
SAMPLING PLAN

Appendix D
SAMPLING PLAN

The following modifications to the sampling plan in the approved QAPP (October 17, 1987) describe procedures and practices to be followed during additional field sampling activities at the Moss-American site. Only those sections of the sampling plan which have been modified are listed below.

2.0 SAMPLE LOCATIONS AND DESIGNATIONS

2.1 SAMPLE LOCATIONS

Sediment Sampling

Seventeen sediment samples will be collected at the proposed locations shown in Figure 1. One sample will be collected at each proposed location, except at locations 1, 2, and 3 where two samples will be collected. In addition to these samples, two duplicates and two blanks will be submitted. Additional river sediment sampling is required to determine representative background concentrations of inorganic and semivolatile compounds (particulates, PAH's, and dioxin) in the Little Menomonee River and Menomonee River downstream of the site.

Six samples and one duplicate will be collected from river sediments in the Little Menomonee River upstream from the site to establish background levels without interference from local road and railway runoff. Three sediment samples will be obtained from the Menomonee River upstream of the confluence of the Little Menomonee River, with a fourth sediment sample collected from an upstream tributary of the Menomonee River. An additional sediment sample will be from nearby Beaver Creek (located near the intersection of Brown Deer Road and 68th Street), which is a different watershed but in a similar urban setting as the Little Menomonee River. Three samples will also be collected from the sediments of tributaries downstream of the site to the Little Menomonee River. These samples will be taken above the influence of high water from the Little Menomonee River.

Finally, three sediment samples will be collected to additionally check for contamination downstream of confluence of the Little Menomonee River and the Menomonee River. These three samples will be collected at a distance of up to one-half mile below the confluence in areas of sediment deposition as determined by a visual survey by walking the river banks or from a small boat.

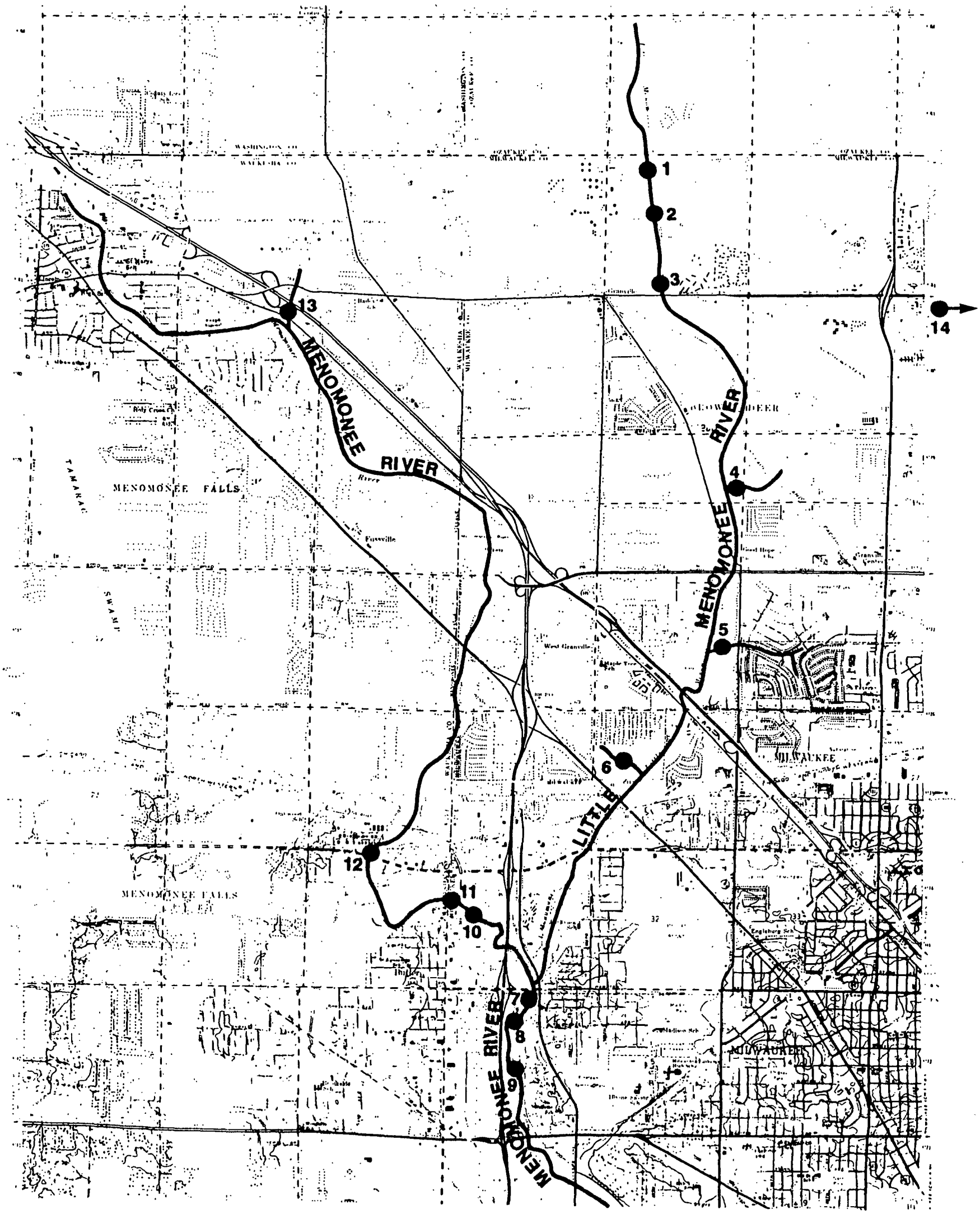

FIGURE 1
PROPOSED SEDIMET SAMPLE LOCATIONS
MOSS-AMERICAN QAPP ADDENDUM 1

Table D-1A
SUMMARY OF SAMPLING AND ANALYSIS PROGRAM AT MOSS-AMERICAN

Laboratory Parameters	DQO Analytical Level	Samples	Field Replicates	Matrix Spike	Matrix Total
Sediment Low-Level PAH (SAS)	V	17	2	1	20
Metals (RAS)	IV	17	2	1	20
SVOCs (RAS)	IV	17	2	1	20
Dioxin	V	17	2	1	20

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