METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY-- DETERMINATION OF ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS IN BOTTOM SEDIMENT BY DUAL CAPILLARY-COLUMN GAS CHROMATOGRAPHY WITH ELECTRON-CAPTURE DETECTION

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CONVERSION FACTORS, ABBREVIATED WATER-QUALITY UNITS, AND ADDITIONAL ABBREVIATIONS AND SYMBOLS

Multiply	_By_	_To obtain_
centimeter (cm)	3.94×10^{-1}	inch
gram (g)	3.53×10^{-2}	ounce, avoirdupois
kilogram (kg)	3.53×10^{1}	ounce, avoirdupois
kilopascal (kPa)	1.45×10^{-1}	pounds per square inch
liter (L)	2.65×10^{-1}	gallon
meter (m)	3.28×10^{0}	foot
microgram (µg)	3.53×10^{-8}	ounce, avoirdupois
microliter (µL)	3.38×10^{-5}	ounce, fluid
micrometer (µm)	3.94×10^{-5}	inch
milligram (mg)	3.53×10^{-5}	ounce, avoirdupois
milliliter (mL)	3.38×10^{-2}	ounce, fluid
millimeter (mm)	3.94×10^{-2}	inch
nanogram (ng)	3.53×10^{-11}	ounce, avoirdupois
nanometer (nm)	3.94×10^{-8}	inch
picogram (pg)	3.53×10^{-14}	ounce, avoirdupois

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = \left[\frac{9 \times °C}{5} \right] + 32.$$

Abbreviated water-quality units used in this report:

µg/kg	microgram per kilogram
ng/g	nanogram per gram

Other units used in this report:

°C/min	degrees Celsius per minute
cm/s	centimeter per second
mg/L	milligram per liter
mL/min	milliliter per minute
ng/µL	nanogram per microliter
pg/µL	picogram per microliter

Other abbreviations and symbols used in this report (also see table 1 for a list of compound abbreviations):

CCV	continuing calibration verification
o,p'-DDD	2,4'-dichlorodiphenyldichloroethane
p,p'-DDD	4,4'-dichlorodiphenyldichloroethane
o,p'-DDE	2,4'-dichlorodiphenyldichloroethene
p,p'-DDE	4,4'-dichlorodiphenyldichloroethene
o,p'-DDT	2,4'-dichlorodiphenyltrichloroethane
p,p'-DDT	4,4'-dichlorodiphenyltrichloroethane
ECD(s)	electron-capture detector(s)
F1	fraction 1
F2	fraction 2
FEP	tetrafluoroethylene-hexafluoropropylene copolymer
GC	gas chromatography
GC/ECD	gas chromatography/electron-capture detection
GC/MS	gas chromatography/mass spectrometry
GPC	gel permeation chromatography
HPLC	high-performance liquid chromatography
ID	internal diameter
K-D	Kuderna-Danish
MDL	method detection limit
MS	mass spectrometric detection
NAWQA	National Water-Quality Assessment
NWQL	National Water Quality Laboratory
PCB(s)	polychlorinated biphenyl(s)
PEM	performance evaluation mix
PTFE	polytetrafluoroethylene
OC(s)	organochlorine(s)
OCIIS	organochlorine internal injection standard
QC	quality control
RPD	relative percent difference
SVOC(s)	semivolatile organic compound(s)
SRM	standard reference material
TPC	third-party check
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UV	ultraviolet

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ABSTRACT

A method for the determination of 30 individual organochlorine pesticides, total toxaphene, and total polychlorinated biphenyls (PCBs) in aquatic bottom sediment is described and laboratory performance data are provided. The method was developed in support of the U.S. Geological Survey's National Water-Quality Assessment program and is based on conventional Soxhlet extraction using dichloromethane. Two aliquots of the sample extract are quantitatively injected onto a styrene-divinylbenzene gel permeation column and eluted with dichloromethane. This gel permeation chromatography step removes inorganic sulfur and large naturally occurring molecules from the sediment extract. The first aliquot is analyzed for semivolatile organic compounds by gas chromatography with mass spectrometric detection. The second aliquot is further split into two fractions by combined alumina/silica adsorption chromatography prior to determination of the organochlorine pesticides and PCBs by dual capillary-column gas chromatography with electron-capture detection (GC/ECD). This report completely describes and is limited to the determination of the organochlorine pesticides and PCBs by GC/ECD. Current (February 1995) data-reporting limits have been set at 1 to 5 micrograms per kilogram for 30 chlorinated pesticides, 50 micrograms per kilogram for total PCBs, and 200 micrograms per kilogram for toxaphene.

INTRODUCTION

Hydrophobic organic contaminants, including many organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs), typically are associated with solids in hydrologic environments. These solids include soils and bottom and suspended sediment and consist of inorganic particles coated with heterogeneous organic matter. Both particle size and the concentration of heterogeneous organic matter influence concentrations of solids-associated contaminants. The method described in this report was devised to extract contaminants from a sediment or soil matrix and isolate the contaminants from

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co-extracted natural organic matter prior to instrumental analysis. For the OC and PCB contaminants, an additional adsorption chromatography step is included to separate the many components of this class into two sample fractions that are more amenable to gas chromatographic analysis, while removing interferences that would compromise the performance of the electron-capture detector used for quantifying these compounds.

This method combines elements of U.S. Geological Survey (USGS) methods O-5104-83 (organochlorine and organophosphorous compounds, recoverable from bottom material) (Wershaw and others, 1987) and O-5116-83 (semivolatile compounds, recoverable from bottom material) (Wershaw and others, 1983). This method incorporates components of U.S. Environmental Protection Agency (USEPA) methods 3540B (Soxhlet extraction), 3640A (gel permeation cleanup), 8080A (OC pesticides and PCBs by gas chromatography), and 8270B (semivolatile organic compounds by capillary column gas chromatography with mass spectrometric detection) (U.S. Environmental Protection Agency, 1992a). It also combines the adsorption chromatography components of USGS method O-5104-83, which is similar to USEPA methods 3610A (alumina column cleanup) (U.S. Environmental Protection Agency, 1990a) and 3630B (silica gel cleanup) (U.S. Environmental Protection Agency, 1992a), into a single combined alumina/silica technique.

There are several advantages of this new method over previously used National Water Quality Laboratory (NWQL) methods. This method has been designed to provide the simultaneous extraction from the sediment sample of 79 other semivolatile organic compounds (SVOCs) that are separately determined using gas chromatography with mass spectrometric detection (GC/MS). This report describes the procedure and documents the performance only for the portion of the method that determines OC pesticides and PCBs by gas chromatography with electron-capture detection (GC/ECD).

The gel permeation chromatography (GPC) step eliminates many co-extracted chemical interferences, reducing chemical noise and improving method detection limits for some compounds. Most importantly, the GPC step removes or greatly reduces the inorganic sulfur in the sediment extract, replacing the more hazardous mercury cleanup procedure of USGS method O-5104-83 (Wershaw and others, 1987). The GPC step also has been miniaturized in relation to USEPA method 3640A (U.S. Environmental Protection Agency, 1992a) so that waste dichloromethane solvent volumes, and the associated disposal costs and health risks, are reduced.

The number of fractions produced by the combined alumina/silica adsorption chromatography step has been decreased to two, halving the number of instrumental analyses required for the OC compounds in relation to USGS method O-5104-83 (Wershaw and others, 1987). Additional compounds also have been added to this method that have not been determined by previous USGS or USEPA methods, reflecting demand by various USGS programs, especially the National Water-Quality Assessment (NAWQA) program.

The sample extraction, cleanup, and the instrumental analysis components of this method, along with the compounds determined by this method, were designed to be similar to method O-9125-94 (chlorinated pesticides, recoverable from aquatic tissue, capillary-column GC/ECD) (Leiker and others, 1995) to facilitate comparison of contaminant concentrations in sediment and tissue samples collected from the same aquatic environment.

Following initial method development, but only partial evaluation of method performance, this method was implemented under routine operation at the NWQL as an unofficial method on January 7, 1993. Subsequently, selected portions of the method were modified to improve performance and reliability. The procedure and performance data detailed below reflect all method improvements that were completely implemented beginning with samples extracted May 19, 1993 (sample set 93139C; *set numbers in this report are provided specifically for the NAWQA program*). The procedural differences and preliminary performance results for the original method, including some matrix-spike sample recovery results, are summarized in Appendix A and are included as a supplement to the partial performance data obtained for the final method. Methodological changes incorporated from January 7 through May 19, 1993, and the resultant impacts on data quality, are briefly summarized in Appendix B specifically for the NAWQA program.

SAFETY CONSIDERATIONS

This method involves the handling of known, suspected, and possibly unknown hazardous chemicals and reagents. The method uses substantial volumes of dichloromethane, a suspected carcinogen, during sample extraction and some extract clean-up steps. The USEPA has special regulations covering the handling and disposal of PCBs. Carefully follow all standard safety practices regarding the use of solvents, compressed gases, OC pesticides, PCBs, polycyclic aromatic hydrocarbons, and other method-related chemicals. Consult material safety data sheets for additional safety information. Always wear appropriate protective clothing, gloves, and eye wear, and use adequate ventilation when preparing samples or standard solutions. Electron-capture detectors (ECDs) contain radioactive [63]nickel and must not be opened by unlicensed operators.

ANALYTICAL METHOD

Organic Compounds and Parameter Codes: Organochlorine pesticides and gross polychlorinated biphenyls, bottom sediment, gas chromatography, O-5129-95 (see table 1)

1. Scope and application

This method is suitable for the determination of 30 individual organochlorine pesticides, as well as total toxaphene, a complex OC pesticide mixture, and total PCBs in soil and sediment samples, with current (February 1995) reporting limits of 1 to 5 micrograms per kilogram (μg/kg) of each individual pesticide, 50 μg/kg of total PCBs, and 200 μg/kg of total toxaphene. This method is applicable to samples of organochlorine pesticides and PCBs that are (1) efficiently extracted from the solid matrix by methanol or dichloromethane, (2) adequately separated from natural co-extracted compounds by gel permeation chromatography, (3) efficiently recovered from the alumina-over-silica adsorption chromatography fractionation step, and (4) sufficiently volatile and thermally stable for gas chromatographic analysis.

2. Summary of method

A 25-g equivalent dry-weight sample is Soxhlet extracted using dichloromethane, reduced in volume, and filtered. Two aliquots of the sample extract are quantitatively injected onto a styrene-divinylbenzene gel permeation column and eluted with dichloromethane. This gel permeation chromatography step removes inorganic sulfur and large natural molecules from the sediment extract. The first aliquot is analyzed for semivolatile organic compounds by gas chromatography with mass spectrometric detection. The second aliquot is further split into two fractions by combined alumina/silica adsorption chromatography prior to determination of the organochlorine pesticides and PCBs by dual capillary-column gas chromatography with electron-capture detection. A flow path of the method is shown in figure 1.

Table 1.--*Common name, abbreviation, codes, and registry number for method compounds*

[NWQL, National Water Quality Laboratory;
CAS, Chemical Abstracts Service; --, none assigned]

Compound common name	Abbreviation	NWQL code	Parameter code	CAS registry number
Aldrin	--	5001	49319	309-00-2
cis-Chlordane	--	5002	49320	5103-71-9
trans-Chlordane	--	5003	49321	5103-74-2
Chloroneb	--	5054	49322	2675-77-6
DCPA (Dacthal)	DCPA	5036	49324	1861-32-1
o,p'-DDD	*o,p'*-DDD	5008	49325	53-19-0
p,p'-DDD	*p,p'*-DDD	5009	49326	72-54-8
o,p'-DDE	*o,p'*-DDE	5010	49327	3424-82-6
p,p'-DDE	*p,p'*-DDE	5011	49328	72-55-9
o,p'-DDT	*o,p'*-DDT	5012	49329	789-02-6
p,p'-DDT	*p,p'*-DDT	5013	49330	50-29-3
Dieldrin	--	5014	49331	60-57-1
Endosulfan I	--	5015	49332	959-98-8
Endrin	--	5018	49335	72-20-8
Heptachlor	--	5020	49341	76-44-8
Heptachlor epoxide (Isomer B)	--	5021	49342	1024-57-3
Hexachlorobenzene	HCB	5006	49343	118-74-1
alpha-Hexachlorocyclohexane	α-HCH	5026	49338	319-84-6
beta-Hexachlorocyclohexane	β-HCH	5027	49339	319-85-7
gamma-Hexachlorocyclohexane	γ-HCH	5022	49345	58-89-9
Isodrin	--	5037	49344	465-73-6
o,p'-Methoxychlor	--	5042	49347	30667-99-3
p,p'-Methoxychlor	--	5044	49346	72-43-5
Mirex	--	5023	49348	2385-85-5
cis-Nonachlor	--	5041	49316	5103-73-1
trans-Nonachlor	--	5039	49317	39765-80-5
Oxychlordane	--	5038	49318	27304-13-8
Pentachloroanisole	PCA	5033	49460	1825-21-4
cis-Permethrin	--	5055	49349	61949-76-6
trans-Permethrin	--	5056	49350	61949-77-7
Polychlorinated biphenyls (total)	PCBs	5024	49459	--
Toxaphene (technical)	--	5025	49351	8001-35-2
Surrogates				
3,5-Dichlorobiphenyl	3,5-DCB	5034	49277	34883-41-5
alpha-Hexachlorocyclohexane-d$_6$	α-HCH-d$_6$	5032	49275	--
2,2',3,4,4',5,6,6'-Octachloro-biphenyl	PCB-204	5048	49276	74472-52-9

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Homogenize wet sediment; centrifuge a portion of
sediment to remove excess water; determine percent
moisture; weigh a 25-gram equivalent dry-weight portion
of centrifuged sediment into beaker

↓

Mix with sodium sulfate to form loose mixture

↓

Transfer to extraction thimble;
add method surrogates; include other quality-control samples

↓

Extract 12 to 16 hours in a Soxhlet apparatus using
methanol wash followed by dichloromethane;
cool; dry extract with sodium sulfate

↓

Reduce extract volume to 3 milliliters (mL) using
Kuderna-Danish (K-D) and nitrogen (N2) gas evaporation;
centrifuge and filter extract; 4-mL extract final volume

↓

Gel permeation chromatography on two aliquots of extract;
collect two different time-window fractions for organochlorine
pesticides and semivolatile organic compounds

Concentrate fraction and solvent
exchange to ethyl acetate using
micro-K-D and N2 gas evaporation;
final volume is 0.5 mL

↓

Add internal injection standard and
analyze by gas chromatography
with full-scan electron-impact
mass spectrometry (GC/MS)

*(Shaded area is specific
to the optional
Semivolatile Organic Compounds
in Bottom Sediment method)*

Reduce fraction and solvent exchange
to hexane using micro-K-D and N2 gas
evaporation; 1.0-mL final volume

↓

Alumina/silica adsorption
chromatography; collect 30 mL hexane
(fraction 1) and 35 mL of 5-percent
acetone in hexane (fraction 2)

↓

Reduce fractions to 0.5 mL using
micro-K-D and N2 gas evaporation;
add internal injection standard

↓

Analyze fractions 1 and 2 by dual
capillary-column gas chromatography
with electron-capture detection
(GC/ECD)

Figure 1.--Flow path for the analytical method.

3. Interferences

Nonmethod organohalogen compounds and other ECD-sensitive compounds that are co-extracted, collected in the GPC fraction, and isolated in the two fractions produced in the alumina/silica adsorption chromatography step are potential interferents. The GC with dual-column confirmation helps minimize chromatographic interferences. For some samples, reliable detection might not be possible because of interferent levels, and reporting limits will have to be raised. Follow-up GC/MS analysis also may be used to verify compound identities if the GC/ECD response is sufficient to suggest adequate detection by GC/MS operated in the electron-impact or electron-capture negative ionization modes. Inorganic sulfur that is incompletely removed during the GPC step can interfere with the analysis of select fraction 1 (F1) compounds, especially some PCB components. High concentrations of a complex mixture might interfere with the determination of individual pesticides or other complex mixtures. For example, high PCB concentrations in F1 might interfere with p,p'-DDE determination. Similarly, high concentrations of toxaphene or technical chlordane components in fraction 2 (F2) will interfere with the determination of other individual F2 pesticides or another F2 complex pesticide mixture (for example, high technical chlordane component concentrations interfering with toxaphene determination). The presence of polychlorinated naphthalenes also might interfere with the determination of PCBs.

4. Apparatus and equipment

The apparatus and equipment required for this method are listed below and grouped by the specific preparation or analysis portions of the method where first used, but these items are not repeated elsewhere in section 4 if used more than once. Specific models and sources that were used for the development or implementation of this method also are listed, as appropriate.

Prior to use, wash all glassware (except class A volumetric glassware) with phosphate-free detergent, rinse sequentially with tap and distilled water, and heat up to 450°C for a minimum of 2 hours. With the exception of vials, micropipet bores, and Pasteur pipets, prerinse all glassware with the solvent used in the procedure requiring the glassware. Clean class A volumetric glassware by rinsing with acetone followed by triple rinsing with pesticide-grade dichloromethane. Solvent-rinsing steps may be substituted for the final heating step for other glassware.

Unless otherwise indicated, prerinse all nonglass items that will be in contact with the sample or sample extract with the solvent used in the procedural step or with pesticide-residue grade acetone.

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4.1 Sample storage, dewatering, and percent moisture determination

4.1.1 *Freezer*--Capable of storing 50 or more 1,000-mL wide-mouth jars at -15 °C.

4.1.2 *Centrifuge*--With 4-place swinging bucket rotor and buckets capable of centrifuging 250-mL centrifuge bottles at up to 5,000 revolutions per minute; International Equipment Co., Model EXD or equivalent.

4.1.3 *Centrifuge bottles*--250-mL capacity made of tetrafluoroethylene-hexafluoropropylene copolymer (FEP).

4.1.4 *Nalgene sealing cap assembly*--For use with FEP centrifuge bottles and fitted with Viton™ O-ring; Nalge Co. or equivalent.

4.1.5 *Toploading analytical balance*--Capable of weighing up to 250 plus or minus (±) 0.1 g.

4.1.6 *Drying balance*--Capable of moisture determination on an approximately 1.5-g aliquot of sediment sample to ±0.1 percent moisture; Sartorius Corp. Thermo Control Balance, Model YTC O1L or equivalent.

4.1.7 *Glass beakers*--400-mL volume.

4.2 Sediment extraction

4.2.1 *Soxhlet apparatus*--85-mL extractor capacity with 45/50 standard taper top joint and 24/40 standard taper bottom joint; fitted with a 500-mL round- or flat-bottom flask and a water-cooled extractor condenser with 45/50 bottom joint.

4.2.2 *Soxhlet extraction sample thimble*--Borosilicate glass, 35 x 90 mm; Kontes, Inc., Model K-586500-0022EC or equivalent.

4.2.3 *Soxhlet extraction combined steam bath/condenser unit*--Organomation Associates, Inc., Model 13055 ROT-X-TRACT or equivalent.

4.2.4 *Fixed volume micropipet*--100- and 200-µL fixed-volume microdispensers.

4.2.5 *Separatory funnel*--1-L.

4.3 Sediment extract concentration

4.3.1 *Kuderna-Danish (K-D) evaporative concentrator*--500-mL reservoir, 3-ball Snyder column, and a special 10-mL centrifuge receiver tube (see 4.3.2).

4.3.2 *Ten-mL centrifuge receiver tube*--Custom made by connecting the top of a 10-mL K-D receiver tube, with 19/22 standard female taper joint, to an 8-cm long by 1.6-cm outside diameter centrifuge tube, volume graduated at 2, 3, and 5 mL; Allen Scientific Glassblowers, Inc., item ASG-215-01 or equivalent.

4.3.3 *Kuderna-Danish combined steam bath/condenser unit*--Organomation Associates, Inc., Model 120 S-EVAP or equivalent.

4.3.4 *Nitrogen gas sample evaporator*--Organomation Associates, Inc., Model 124 N-EVAP or equivalent.

4.4   Sample extract filtration

4.4.1 *Centrifuge*--International Equipment Co., Model HN-SII or equivalent.

4.4.2 *Syringe*--5- or 10-mL gas-tight or ground-glass syringe equipped with Luer-Lok™ fitting.

4.5   Gel permeation chromatography

4.5.1 *Gel permeation chromatography system*--An automated GPC system consisting of the following components, all from Waters Corp. or equivalent:

4.5.1.1 *High-performance liquid chromatography (HPLC) pump*, Model 501.

4.5.1.2 *Autosampler*, Model 717 with 2-mL injection loop capacity and tray storage region maintained at 20°C.

4.5.1.3 *Absorbance detector*, Model 441 with excitation wavelength set at 254 nm.

4.5.1.4 *Data module and integrator*, Model 746.

4.5.1.5 *Fraction collector*, no model number, fitted with in-house built tube holder capable of holding 36 25-mL K-D receiver tubes.

4.5.1.6 *HPLC in-line precolumn filter unit*, Model WATO84560 with replaceable 0.2-μm filters.

4.5.2 *Column heater*--Set at 27.0°C; Jones Chromatography Ltd. or equivalent.

4.5.3 *Nitrogen pressurization system*--Consists of a regulated grade 5 nitrogen source, PTFE tubing, a 23-gage needle, and associated metal fittings and Vespel™ ferrule for connecting the needle to the nitrogen source via the tubing.

4.5.4 *Helium sparging system*--Use for deoxygenating the dichloromethane solvent prior to GPC.

4.5.5 *HPLC pump priming syringe*--25-mL, Hamilton Gas-Tight 1000 Series, Model 82520 or equivalent.

4.5.6 *Balance*--Capable of weighing up to 200 ± 0.0001 g.

4.5.7 *K-D receiver tube*--Calibrated to 25-mL volume, with 19/22 ground-glass stopper.

4.6 GPC fraction concentration and solvent exchange

4.6.1 *Water bath*--Precision Scientific Co., Model 82 or equivalent, fitted with a rack capable of holding at least 18 25-mL receiver tubes.

4.6.2 *Micro-Snyder column*--3-ball.

4.7 Adsorption chromatography cleanup and fractionation

4.7.1 *Nitrogen head-pressure system*--An eight-column position, in-house built system designed to deliver nitrogen gas head pressure from 0 to 70 kilopascals (kPa) gage pressure and to allow precise and accurate control of solvent flow at 1 mL/min through each column at less than 70 kPa of back pressure. The system uses eight Norgren Model 11-018-146 relieving regulators or equivalent, fitted with pressure gages, along with associated hardware to connect the regulators to the columns, including 3.2-mm internal diameter (ID) PTFE tubing, shut-off valves, tubing fittings, and pinch clamps. The system also includes a molecular sieve/activated-charcoal filter that is used to purify the nitrogen gas, and an in-house-built eight-position rack for holding the 40-mL K-D receiver tubes.

4.7.2 *Glass chromatographic cleanup column*--30-cm long by 10-mm ID fitted with coarse glass frit, Teflon™ stopcock, solvent reservoir top capable of holding at least 60 mL of solvent, and fitted with a 28/15 female ball joint for connection to the nitrogen head-pressure system (4.7.1) via a 28/15 male ball joint; Allen Scientific Glassblowers, Inc., items ASG-201-01 and ASG-202-01 or equivalent.

4.7.3 *K-D receiver tube*--Custom-made 40-mL tube that uses a 25-mL K-D receiver tube modified with a top reservoir capable of containing at least 40 mL of solvent and graduated at 30, 35, and 40 mL. The tube has a 19/22 joint; Allen Scientific Glassblowers, Inc., item ASG-210-01 or equivalent.

4.7.4 *Bottle-top solvent dispenser*--5- or 10-mL; Brinkmann Dispensette or equivalent.

4.8 Fraction concentration

    4.8.1 *Syringe*--10-µL volume for addition of internal injection standard solution.

4.9 Gas chromatography/electron-capture detector analysis

    4.9.1 *Gas chromatograph*--Hewlett-Packard 5890 or Perkin-Elmer Autosystem, equipped with two electron-capture detectors, an autosampler, a split/splitless injector, and a computer controller with Perkin-Elmer's Turbochrome 3.3 chromatography software, or equivalent system. The system needs to be suitable for use with single injection, dual capillary-column GC analysis.

    4.9.2 *Syringe*--10-µL volume; Hamilton Co., number 80377 for GC autosampler or equivalent.

4.10 Instrument calibration and spike standard solutions preparation

    4.10.1 *Volumetric flasks*--Class A, varied volumes from 1- to 1,000-mL graduation.

    4.10.2 *Micropipets*--25- to 250-µL fixed- and variable-volume pipets.

    4.10.3 *Syringes*--Variable volumes from 10- to 500-µL.

5. Reagents and consumable materials

The reagents and consumable materials required for this method are listed below and grouped by the specific preparation or analysis portions of the method, but are not repeated if used more than once. Specific models and sources that were used for the development or implementation of this method also are listed, as appropriate.

5.1 Sample storage, dewatering, and percent moisture determination

    5.1.1 *Sample containers*--Glass, wide-mouth, 1,000 mL, with PTFE-lined lids.

    5.1.2 *Weighing boats*--Disposable, aluminum, 5.1-cm diameter.

    5.1.3 *Sodium sulfate*--Anhydrous, granular, reagent grade, heat at 450°C for 8 hours, and store in a ground-glass stoppered flask in a desiccator until used.

5.2 Sediment extraction

5.2.1 *Solvents*--Dichloromethane and methanol, pesticide-residue grade or higher purity.

5.2.2 *Boiling chips*--Pre-extract with dichloromethane and heat at 450°C for 2 hours. Store in a sealed jar until used.

5.2.3 *Disposable glass capillaries*--For 10-, 25-, 50-, 100-, 200-, and 250-μL micropipets. Clean glass capillaries by heating at 350°C for 2 hours.

5.2.4 *OC surrogate solution*--Contains 3,5-dichlorobiphenyl (3,5-DCB), 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB-204), and deuterium-labeled *alpha*-hexachlorocyclohexane (α–HCH-d$_6$). Commercially obtained intermediate-concentration solutions were diluted to a final surrogate solution concentration (C_a) of 2 ng/μL of each component in hexane. Other appropriate surrogate compounds may be added or substituted into this method after demonstrating acceptable method performance.

5.2.5 *Individual OC pesticide spike solution*--Contains the individual OC pesticides listed in table 1, commercially obtained at intermediate concentrations, which were diluted to a final spike solution concentration (C_b) of 2 ng/μL of each component in hexane.

Note: n-Hexane is the suggested solvent for preparing all surrogate and spike (and calibration) solutions to help ensure proper compound dissolution, especially of the higher molecular-weight OC compounds. Methanol, and solvents of similar polarity, are not suggested because many of the OC compounds, like the PCB-204 surrogate, are not readily soluble in methanol. Also, use of some higher boiling intermediate polarity solvents (for example, toluene or ethyl acetate) in the spiking solutions might result in fraction irreproducibilities during the adsorption chromatography step.

5.2.6 *PCB spike solution*--Contains one or more Aroclor™ PCB standard (for example, 1242, 1254, and 1260) at a concentration of at least 25 ng/μL for each Aroclor in hexane. The grade of Aroclor stock standard solutions was that obtained from Supelco, Inc.

5.2.7 *Toxaphene spike solution*--100 ng/μL in hexane. The grade of toxaphene stock standard solutions was that obtained from Supelco, Inc.

5.2.8 *Standard reference materials (SRMs) or other quality-control (QC) reference materials*--Any SRM, round-robin, or other sediment or soil reference material available to test the method for recovery of some or all of the method compounds may be an appropriate QC material. Materials tested for this method and found to be at least partially suitable include the following:

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5.2.8.1 *SRM 1941*, National Institute of Standards and Technology's (NIST) Organics in Marine Sediment SRM. (Note: SRM 1941a renewal became available in 1994 and should be a suitable replacement for SRM 1941.)

5.2.8.2 *Semivolatiles in Soil QC Material*, Environmental Resource Associates' PriorityPollunT™ spiked soil, catalog number 720.

5.3 Sediment extract concentration

5.3.1 *Nitrogen gas*--For solvent evaporation, grade 5 or equivalent.

5.4 Sample extract filtration

5.4.1 *Filter*--0.2-μm pore size, 25-mm diameter disposable PTFE membrane syringe filter; Gelman Sciences Acrodisc™ CR or equivalent.

5.4.2 *Pasteur pipets*--14.6- and 22.9-cm-long disposable pipets with rubber bulbs.

5.4.3 *GPC vial*--4-mL, with open-top screw-cap and PTFE-faced silicone rubber septum; Supelco, Inc., part numbers 2-3219M, 2-3261M, and 3-3185M or equivalent.

5.5 Gel permeation chromatography

5.5.1 *Helium gas*--Grade 5 or equivalent.

5.5.2 *GPC columns*--Two 30-cm-long by 7.5-mm ID columns packed with 5-μm diameter PGel™ styrene-divinylbenzene resin particles having 50-angstrom pore size; Polymer Laboratories, Ltd. or equivalent. The columns are connected in series with a low dead-volume union.

5.5.3 *GPC OC fraction test solution*--Contains *trans*-permethrin, hexachlorobenzene, and elemental sulfur each at a maximum concentration of 200 pg/μL in dichloromethane.

5.6 GPC fraction concentration and solvent exchange

5.6.1 *Hexane*--Pesticide-residue grade or higher purity.

5.7 Adsorption chromatography cleanup and fractionation

5.7.1 *Alumina*--Woelm Alumina N Activity I, 50 to 200 mesh; Scientific Adsorbents, Inc., catalog number 02087, lot number 50504 (see section 7.7 note).

5.7.2   *Silica gel*--Woelm Active, 100 to 200 mesh; Scientific Adsorbents, Inc., catalog number 02747, lot number 50419 (see section 7.7 note).

5.7.3   *Acetone and water*--Pesticide-residue grade or higher purity.

5.7.4   *Fraction 2 elution solvent*--Prepare at least 750 mL of a 5-percent acetone and 95-percent hexane solution.

Note: Carefully prepare the 5-percent acetone and 95-percent hexane solution. Slight variations from the specified mixture composition might result in unwanted errors in the alumina/silica fractionation process.

5.8   Fraction concentration

5.8.1   *Vial*--1.8- or 2-mL, amber glass, with aluminum crimp caps that have dual PTFE-faced silicone rubber septum.

5.8.2   *OC internal injection standard (OCIIS) solution*--Contains tetrachloro-*m*-xylene and decachlorobiphenyl at 10 ng/µL in hexane.

5.9   Gas chromatography/electron-capture detector analysis

5.9.1   *Capillary GC columns.*

5.9.1.1   *Primary column*, fused-silica, 30-m by 0.25-mm ID, internally coated with a 5-percent diphenyl- and 95-percent dimethyl-polysiloxane stationary phase having a 0.25-µm film thickness; Restek Corp. Rtx-5™ or equivalent.

5.9.1.2   *Secondary column*, fused-silica, 30-m by 0.25-mm ID, internally coated with a 14-percent cyanopropylphenyl- and 86-percent dimethyl-polysiloxane stationary phase having a 0.25-µm film thickness; Restek Corp. Rtx-1701™ or equivalent.

5.9.2   *Column connector*--Glass Y-type; Restek Corp. number 20405 or equivalent.

5.9.3   *GC guard column*--Uncoated fused-silica tubing, 5-m by 0.32-mm ID; Restek Corp. number 10044 or equivalent.

5.9.4   *GC injection-port liners*--glass. Use any instrument-specific splitless or direct injection-port liner that provides minimal breakdown of endrin, *p,p'*-DDT, and *p,p'*-methoxychlor following deactivation with a silanization reagent, and that provides acceptable peak shape and detector response.

5.9.5   *Silanizing reagent*--For deactivating GC injection-port liners; Supelco, Inc. Sylon CT or equivalent.

5.10 GC/ECD calibration and quality-control solutions

Note: Prior to analysis, add 10 µL of the OCIIS solution (5.8.2) to each of the GC calibration (5.10.1) and quality-control (5.10.2) solutions listed below. Make sure to exactly match the lot number or NWQL standard solution number of the OCIIS solution that will be added to the sample extracts under section 7.8.5. The OCIIS solution must be added to a known volume (for example, 200 µL) of calibration solution to allow for compound dilution correction and to allow for use of internal standard quantitation (see section 9.1).

5.10.1 *GC calibration standard solutions.*

5.10.1.1 *OC pesticide standard solutions*--Prepare working standard solutions of the entire suite of individual OC compounds listed in table 1 at 5, 10, 20, 50, 100, and 200 pg/µL in hexane using commercially prepared higher concentration, single- or mixed-compound stock solutions.

5.10.1.2 *PCB calibration standard solution*--In this method, total PCBs typically were determined using a single concentration mixed Aroclor PCB calibration standard solution. This solution contains a 1:1:1 mixture of Aroclor 1242, 1254, and 1260 at 200 pg/µL each in hexane. Additional solutions at other concentrations may be used to produce a multipoint calibration curve. The grade of Aroclor stock standard solutions was that obtained from Supelco, Inc.

5.10.1.3 *Toxaphene calibration standard solution*--In this method, total toxaphene typically was determined using a single calibration standard solution of technical toxaphene at 800 pg/µL. Additional solutions at other concentrations may be used to produce a multipoint calibration curve. The grade of toxaphene stock standard solutions was that obtained from Supelco, Inc.

5.10.2 *GC quality-control (QC) solutions.*

5.10.2.1 *Performance evaluation mix (PEM)*--Use PEM to monitor for degradation of problem compounds in the GC injection port. Typically contains *p,p'*-DDT (100 pg/µL), endrin (50 pg/µL), and *p,p'*-methoxychlor (250 pg/µL) at a minimum; Supelco, Inc. pesticide PEM number 4-8397 or equivalent.

5.10.2.2 *Continuing calibration verification (CCV) standard solution*-- CCV is identical to the midpoint calibration standard, typically the 50-pg/µL standard. Analyze the CCV after every five set samples, preceding the PEM, to verify the initial calibration (see table 6 later in report).

5.10.2.3 *Third-party check (TPC) solution*--An independent, commercially prepared standard solution which is used to verify the accuracy of the concentrations of the calibration standard components. If possible, the TPC concentration should be equivalent to the CCV concentration.

6. Collection, shipment, and storage of sediment samples

6.1 Sampling methods and sample-collection equipment

Use sampling methods that are capable of collecting bed-sediment samples that accurately represent the organic contaminant composition of bed sediment at a given location and time. Use sample-collection equipment that is free of plastic tubing, gaskets, and other parts that might leach interferences, sorb contaminants, or abrade, and, thus, contaminate sediment samples. Detailed descriptions of sampling methods and equipment (including equipment cleaning procedures) used to collect representative bed-sediment samples for organic contaminants are provided in Edwards and Glysson (1988), and, specifically for the USGS National Water-Quality Assessment program, in Shelton and Capel (1994).

6.2 Sample shipment

Place collected samples into 1,000-mL wide-mouth glass jars with PTFE-lined lids or other approved containers and store on ice until shipment. Ship samples on ice via overnight carrier to the laboratory as soon as possible following collection.

6.3 Sample storage

Upon receipt at the laboratory, carefully decant excess water above the sediment layer and store the samples at -15°C until analysis. Sample holding times for this method have not been established.

7. Sample Preparation Procedure

Samples are usually organized into sets of 16 total samples, including QC samples, because two extraction units or nitrogen head-pressure systems for adsorption chromatography accommodate 16 samples. Typically, 11 to 12 field samples are included in a set, depending on the number of laboratory QC samples.

7.1 Sample dewatering and percent moisture determination

7.1.1 Retrieve samples from the freezer and allow to thaw.

7.1.2 Thoroughly homogenize each sample with a spatula.

7.1.3 Remove an approximately 20-g wet-weight aliquot to an appropriate container for separate determination of total carbon and total inorganic carbon (Wershaw and others, 1987); obtain total organic carbon by difference.

7.1.4   Weigh approximately 150 g of mixed sample into a tared 250-mL centrifuge bottle and record sediment weight (W_a). Repeat with a second sample identically weighing to ±0.1 g of the first sample for balanced centrifuge operation. Repeat for two more samples and centrifuge (4.1.2) the two sets of paired samples (4 total) for 20 minutes at 2,000 revolutions per minute. Carefully decant the clear supernatant water; pipet the supernatant using a Pasteur pipet if the sediment pellet is too soft. If the supernatant is not clear, repeat centrifugation before decanting. Record weight of sediment after decanting water (W_b).

7.1.5   Thoroughly rehomogenize the sediment sample in the centrifuge bottle. Determine the percent moisture content to ±0.1 percent of a 1.5- to 2.2-g aliquot of the centrifuged sediment using the drying balance (4.1.6). The wet-weight fraction (f_w) of the centrifuged sediment = percent wet weight/100.

Calculate the dry-weight fraction of centrifuged sediment (f_d):

$$f_d = 1 - f_w$$

7.1.6   Weigh an amount of wet, centrifuged sediment needed to produce a 25-g equivalent dry-weight sample into a tared 400-mL beaker.

Weight of wet sediment needed for extraction = 25 g/f_d

Record sediment wet weight (W_w) to ±0.1 g.

7.1.7   Add anhydrous sodium sulfate to the beaker in an amount equivalent to approximately four times the amount of water present in the sediment. The total amount of sediment-sodium sulfate mixture must not exceed 160 g, otherwise the mixture will not fit completely within an extraction thimble (7.2.1):

Weight of sodium sulfate needed = $W_w \times f_w \times 4$

where W_w = wet-sediment weight, in grams (7.1.6); and
             f_w = wet-weight fraction of sediment (7.1.5).

Mix thoroughly, and, if necessary, add more sodium sulfate to ensure that the mixture is dry and loose.

7.2   Sediment extraction

7.2.1   Add the sediment-sodium sulfate mixture to a Soxhlet extraction thimble. Repeat for all samples.

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Note: If the entire sediment-sodium sulfate mixture will not fit into a thimble, repeat steps 7.1.6 and 7.1.7 using less sediment.

7.2.2   Prepare the following QC samples as required, depending on the types of analyses to be performed.

7.2.2.1   Laboratory blank (reagent blank) -- Place 125 g sodium sulfate into an extraction thimble. <u>Optional blank matrix</u>: Use 25 g of clean sand (baked at 600°C for 8 hours) as the matrix, mixed with approximately 100 g sodium sulfate.

7.2.2.2   Reagent OC spike sample -- Place 125 g sodium sulfate into an extraction thimble, place thimble into Soxhlet, and spike sodium sulfate with 100 µL (V_b) of individual OC pesticide spike solution (5.2.5) using a micropipet or syringe. <u>Optional spike matrix</u>: Use 25 g of clean sand as the matrix and mix with approximately 100 g sodium sulfate. <u>Optional or additional spike sample types</u>: Either along with or in place of the reagent OC spike sample, include a reagent PCB spike (5.2.6) or reagent toxaphene spike (5.2.7) sample as desired. Preparation of a spike sample containing more than one spike solution generally is not recommended because of the complexity of the PCB and toxaphene mixtures.

7.2.2.3   Standard reference material (SRM) sample -- Place 4 to 25 g of appropriate SRM (see 5.2.8) into an extraction thimble; the amount extracted will depend on SRM availability, compound concentrations relative to the reporting level, and cost. Mix in 20 to 100 g sodium sulfate to simulate step 7.1.7. (The SRMs usually do not contain much water.)

7.2.3   Extract and process the QC samples through the remainder of the method exactly like the field-sediment samples.

7.2.4   Place the extraction thimble into a Soxhlet connected to a 500-mL flask containing 350 mL dichloromethane and 5 to 10 boiling chips.

7.2.5   Add 100 µL (V_a) of OC surrogate solution (5.2.4) on top of each sample contained in a thimble using a micropipet or syringe.

7.2.6   Carefully add 25 mL methanol to the top of the sample and allow 20 minutes for the solvent to percolate through sample to the thimble frit. This step helps to remove any residual moisture not bound by the sodium sulfate.

Note: Do not use more than 25 mL of methanol during this step. The amount of methanol added must not exceed 7 percent of the total volume of dichloromethane plus methanol used during the extraction (see 7.3.2 note).

7.2.7   Attach the Soxhlet to the condenser and extract the sample at 70°C for 12 to 16 hours.

7.2.8   Following extraction, add about 50 g sodium sulfate to the flask and swirl to remove residual water. Add more sodium sulfate as needed to ensure water removal. Excessive water may require removal using a 1-L separatory funnel.

7.3   Sediment extract concentration

7.3.1   Transfer the extract (but not the sodium sulfate) from the flask to a K-D concentrator (4.3.1) fitted with a 10-mL centrifuge receiver tube (4.3.2) containing 5 to 10 boiling chips. Rinse the flask three times using 5 to 10 mL of dichloromethane each and transfer the rinses to the K-D concentrator.

7.3.2   Concentrate the extract to about 4 to 6 mL at 70°C.

Note: The methanol used in the extraction step must be removed during this K-D concentration step, otherwise it will cause problems during the GPC cleanup (7.5). Methanol is completely removed only by the formation of an azeotrope having a 92.7 percent dichloromethane and 7.3 percent methanol composition that boils at 37.8 °C (at 101.3 kPa). Therefore, the amount of methanol must not exceed 7 percent of the total extract volume of dichloromethane plus methanol in the Soxhlet extract (7.3.1); otherwise, the desired azeotrope composition will not occur during the K-D concentration (see 7.2.6 note).

7.3.3   Further reduce the extract to 3.0 mL using a gentle stream of nitrogen gas (4.3.4). Store extract at 4°C until step 7.4.

7.4   Sediment extract filtration

7.4.1   Centrifuge (4.4.1) paired sets of extracts, contained in uncapped centrifuge receiver tubes, at 2,150 revolutions per minute for 10 minutes.

7.4.2   Weigh a labeled, 4-mL GPC vial with cap and septum attached (5.4.3) to ±0.0001 g and record weight (W_v).

7.4.3   Attach a 0.2-µm PTFE filter (5.4.1) to a 5-mL Luer-Lok syringe. Remove syringe plunger and place tared GPC vial under filter-tip outlet.

7.4.4   Transfer the centrifuged extract to the syringe barrel using a Pasteur pipet, taking care not to dislodge the centrifuged solids.

7.4.5   Carefully insert plunger into syringe and pass the extract through the filter into the GPC vial. After expelling sample, push air through the filter to remove residual extract from the filter.

7.4.6 Rinse the centrifuge receiver tube with 500 μL dichloromethane, washing down the tube walls using the Pasteur pipet. Transfer the rinse (including disrupted centrifuged solids) to the syringe barrel using the Pasteur pipet. Filter rinse into GPC vial as in 7.4.5.

7.4.7 Repeat step 7.4.6.

7.4.8 Bring extract volume up to 4 mL with dichloromethane and cap GPC vial. Store extract at 4°C until step 7.5.

7.5 Gel permeation chromatography

Complete details of GPC operation are beyond the scope of this report. The following procedure outlines the steps necessary for GPC instrument fraction calibration and subsequent cleanup of sample extracts. Consult the appropriate instrument manuals for additional details regarding general GPC system operation.

7.5.1 The GPC data system should remain on continuously; turn on other system components, including the pump, autosampler, detector, fraction collector, and column heater, at least 2 hours in advance of fraction calibration.

7.5.2 Degas the dichloromethane mobile phase with helium gas for 30 minutes prior to use.

7.5.3 Pump degassed dichloromethane through the GPC columns at the mobile phase flow rate of 1 mL/min (see note) for at least 2 hours prior to fraction calibration (7.5.8). *Note: Slowly ramp up the flow rate from 0.1 to 1 mL/min over a 5-minute period to minimize pressure shock to the GPC columns.*

7.5.4 Bring the GPC vial containing the sample to room temperature.

7.5.5 Just prior to vial pressurization (7.5.6), weigh each extract contained in the capped GPC vial to ±0.0001 g and record weight (W_G). Calculate the weight of extract before GPC (W_1) from

$$W_1 = W_G - W_v \tag{1}$$

where W_G = weight of extract and capped vial before GPC , in grams (7.5.5); and

W_v = weight of empty, capped vial, in grams (7.4.2).

Note: The actual amount of extract injected into the GPC system will be determined by weight difference before and after GPC injection (see 7.5.10).

7.5.6   The headspace of all sample extracts and GPC test solutions contained in 4-mL GPC vials must be pressurized with nitrogen gas to assist in syringe withdrawal of the extract and test-solution aliquots for injection into the GPC. Pierce the vial septum with the pressurization needle, and pressurize with 200 kPa nitrogen for 1 minute. **CAUTION: Do not place the needle into the liquid.** Rinse the needle with dichloromethane between vial pressurizations.

7.5.7   Establish GPC system cleanliness and baseline stability by injecting 1,100 µL dichloromethane (system blank) and monitoring detector response at low attenuation (for example, at attenuation 8). Fractions typically are not collected for GPC system blank runs.

7.5.8   GPC fraction calibration -- Compound elution times may vary within or between analyses of sample sets because of GPC column aging, the presence of residual methanol from sample extraction, and possibly other factors. Prior to beginning a GPC autosequence, establish the fraction collection times for the OC compounds to allow final configuration of the fraction collector.

7.5.8.1   Establish OC fraction collection times by injecting 1,100 µL of the GPC OC fraction test solution (5.5.3) and monitoring the elution times of the peaks at low attenuation. Repeat injections of the GPC OC fraction test solution as necessary to ensure chromatographic reproducibility. Typically, fractions are not collected for the GPC OC fraction test solution.

7.5.8.1.1   Set the "start time" on the fraction collector for the GPC OC fraction at least 10 seconds earlier than the beginning of the *trans*-permethrin peak (the first OC compound that elutes from the GPC; see fig. 2).

Note: Large natural substances that are being removed from the extract during the GPC step mostly elute prior to the method compounds. Therefore, do not set the collection "start time" much earlier than about 20 seconds before the beginning of the trans-permethrin peak; otherwise, the natural material may not be successfully eliminated from the collected fraction.

7.5.8.1.2   Set the "end time" on the fraction collector for the GPC OC fraction at least 10 seconds later than the end time of the hexachlorobenzene (HCB) peak (the last OC compound that elutes from the GPC; see fig. 2).   The HCB peak should be at least baseline separated from the sulfur peak, otherwise there might be some sulfur detected during GC/ECD analysis. Very small amounts of sulfur carry over into the collected OC GPC fraction usually will result in a small sulfur peak in the GC/ECD that typically does not interfere with the determination of any compounds (except for select individual PCB congeners). Carryover of larger amounts of sulfur might result in a large, broad peak or a severe baseline rise in the GC/ECD chromatogram, which might interfere with compound determinations. Thus, it is important to establish GPC conditions and set up OC fraction collection times so that sulfur is eliminated (or at least greatly minimized) in the collected GPC OC fraction.
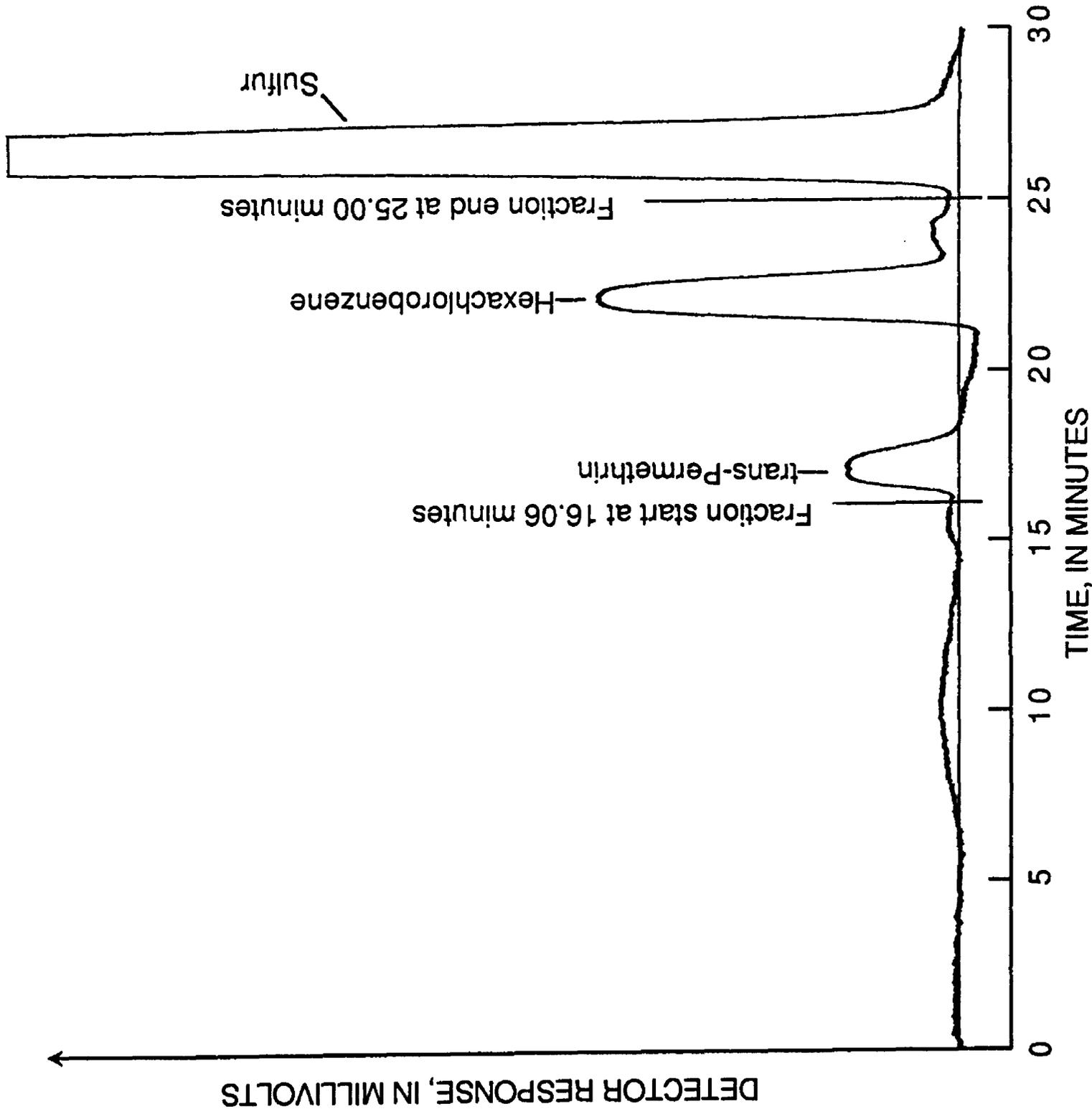
Figure 2.--Gel permeation chromatogram of the fraction test solution at attenuation 8 showing analyst-determined start and end times for the organochlorine pesticide fraction. Chromatographic conditions are given in text.

7.5.9   Perform a GPC autosequence cleanup of the samples. Inject 1,100 µL of the sample extract and collect the GPC OC fraction in a 25-mL K-D receiver tube. Use a 30-minute total separation time per sample. Table 2 lists a suggested autosequence assuming one reagent blank, reagent OC spike, and SRM sample, 12 field samples, and one field sample duplicate. Repeated injections of the GPC OC fraction test solution and the system blank helps ensure continued fraction calibration and system cleanliness.

Table 2.--*Suggested gel permeation chromatography (GPC) autosequence*

Sequence	Sample type
1	System blank (7.5.7)
2	Reagent blank (7.2.2.1)
3	Reagent OC spike (or set spike options, 7.2.2.2)
4	Sample 1
5	Sample 2
6	Sample 3
7	GPC OC fraction test solution (5.5.3)
8	System blank
9	Sample 4
10	Sample 5
11	Sample 6
12	Sample 7
13	Sample 8
14	GPC OC fraction test solution
15	System blank
16	Sample 9
17	Sample 10
18	Sample 11
19	Sample 12
20	Sample duplicate
21	Standard reference material samples (7.2.2.3)
22	GPC OC fraction test solution
23	System blank

7.5.10   Reweigh the GPC sample vial with original cap and septum to ±0.0001 g (W_H) as soon as possible after injection of the sample or following completion of an overnight automated analysis, and calculate the weight of OC extract processed through the GPC (W_2):

$$W_2 = W_G - W_H \qquad (2)$$

where W_G = weight of extract and vial before GPC, in grams (7.5.5); and
    W_H = weight of extract and vial after GPC, in grams (7.5.10).

7.5.11 Cap K-D receiver tube containing the GPC OC fraction and refrigerate until the concentration step (7.6).

7.5.12 Replace the septum on the GPC sample vial and store the remaining portion of the extract not processed through the GPC in a freezer for subsequent GPC injection for collection of a separate fraction for SVOC analysis or re-analysis of an OC fraction.

7.6 GPC OC fraction concentration and solvent exchange

7.6.1 Add 4 mL hexane and two to three small boiling chips to the GPC extract, and attach a 3-ball micro-Snyder column to the top of the K-D receiver tube.

7.6.2 Slowly introduce the K-D receiver tube to a water bath (4.6.1) maintained at 70°C, and reduce the solvent volume to about 4 mL, or until solvent evaporation dramatically decreases. Remove the tube from the bath and cool.

7.6.3 Raise bath temperature to 85 to 87°C. Add two to three fresh boiling chips and 1 mL hexane to the K-D receiver tube, vortex, and place into water bath for about 20 minutes. Do not reduce solvent volume to less than 1 mL.

7.6.4 Remove tube from water bath and reduce the extract to 1 mL using a gentle stream of nitrogen (4.3.4). Cap and store samples at 4°C until adsorption chromatography step (7.7).

7.7 Adsorption chromatography cleanup and fractionation

This procedure removes additional unwanted interferences, and, more importantly, separates the PCB components from the majority of the technical chlordane and toxaphene components. Table 3 lists the recoveries of method compounds measured in alumina/silica fractions 1 and 2 on the basis of column spike experiments.

Note: The adsorption chromatography procedure was developed and characterized using the specific lots of alumina and silica listed in section 5.7 at the specified levels of heat activation and water deactivation (7.7.1 and 7.7.2). Use of different sources of sorbents or even different lots from the same source requires reverification of the fractionation recoveries to ensure acceptable elution volumes for all of the method compounds prior to routine use on samples. Reverify fraction recoveries using column spikes of the method compounds in hexane.

Table 3.--*Mean percent recovery of method compounds in alumina/silica fraction from two- to eight- column-spike experiments*

[±, plus or minus; --, not detected]

Compound[a]	Mean recovery ± standard deviation	
	Fraction 1[b] (percent)	Fraction 2[c] (percent)
Aldrin	97 ± 6	--
cis-Chlordane	--	96 ± 8
trans-Chlordane	--	89 ± 11
Chloroneb	--	118 ± 57
DCPA (Dacthal)	--	92 ± 6
o,p'-DDD	1	84 ± 15
p,p'-DDD	--	104 ± 4
o,p'-DDE	31 ± 8	60 ± 14
p,p'-DDE	92 ± 8	6 ± 1
o,p'-DDT	11 ± 6	74 ± 15
p,p'-DDT	--	88 ± 11
Dieldrin	--	83 ± 13
Endosulfan I	--	91 ± 3
Endrin	--	88 ± 7
Heptachlor	85 ± 7	6 ± 2
Heptachlor epoxide	--	94 ± 10
Hexachlorobenzene	94 ± 10	1 ± 1
alpha-Hexachlorocyclohexane	--	102 ± 16
beta-Hexachlorocyclohexane	--	77 ± 16
gamma-Hexachlorocyclohexane	--	106 ± 21
Isodrin	95 ± 9	2 ± 1
o,p'-Methoxychlor	--	99 ± 6
p,p'-Methoxychlor	--	92 ± 11
Mirex	96 ± 8	2 ± 2
cis-Nonachlor	--	108 ± 10
trans-Nonachlor	3 ± 2	89 ± 10
Oxychlordane	--	97 ± 6
Pentachloroanisole	8 ± 8	103 ± 26
cis-Permethrin	--	99 ± 12
trans-Permethrin	--	106 ± 5
Polychlorinated biphenyls (total)	(d)	(d)
Toxaphene (technical)	8 ± 2	90 ± 2
Surrogates		
3,5-Dichlorobiphenyl	93 ± 10	--
PCB-204	91 ± 5	--
alpha-HCH-d$_6$	--	100 ± 8

[a]The individual pesticides were spiked at 100 nanograms per column; toxaphene at 5

microgroms per column; 3,5-dichlorobiphenyl at 300 nanograms per column; PCB-204 at 60 nanograms per column; and *alpha*-HCH-d$_6$ at 70 nanograms per column.

^{b}Fraction 1 is 30 mL of hexane. The number of observations (n) for the fraction 1 compounds was 8, except for *o,p'*-DDD (n=1), *trans*-nonachlor (n=5), pentachloroanisole (n=6), toxaphene (n=2), 3,5-dichlorobiphenyl (n=3), and PCB-204 (n=3).

^{c}Fraction 2 is 35 mL of 5-percent acetone and 95-percent hexane. The number of observations (n) for the fraction 2 compounds was 3, except for *trans*-permethrin (n=1) and toxaphene (n=2).

^{d}Fraction recoveries were not determined for PCBs in these tests. PCBs were detected almost exclusively in fraction 1 at recoveries typically greater than 85 percent in earlier tests using slightly different elution solvent conditions.

7.7.1   Sorbent activation

7.7.1.1   Weigh into a 500-mL Erlenmeyer flask two times the total amount of alumina (or silica gel) required to process one set of samples.

Recommended amount of alumina $= 2 \times (3 \text{ g} \times \text{ number of samples})$

Recommended amount of silica gel $= 2 \times (5 \text{ g} \times \text{ number of samples})$

Activate the sorbents for at least 12 hours in an oven at 150°C. Store sorbents in the 150°C oven until ready to begin deactivation.

7.7.2   Sorbent deactivation

7.7.2.1   Following activation, place the unstoppered flasks in a desiccator and allow the sorbents to cool to room temperature.

7.7.2.2   Sorbents are deactivated on a weight-to-weight basis using high-purity water. Alumina is 8.5-percent deactivated, and silica gel is 2-percent deactivated. For example, if 100 g of 8.5-percent deactivated alumina is desired, weigh 91.5 g of alumina into a 500-mL Erlenmeyer flask and add 8.5 g water using a Pasteur pipet. Immediately cap the flask with ground-glass stopper and vigorously shake by hand for 10 minutes.

Note: Minimize contact of the sorbent to ambient air since the sorbents rapidly adsorb air moisture which can affect the level of deactivation.

Sorbent Reusage Note: Unused deactivated sorbents may be reused at a later time; simply reactivate the unused portion at 150 °C (7.7.1).

7.7.2.3.   Place flasks on a mechanical shaker for 2 hours to equilibrate.

7.7.3 Dry pack the chromatography columns in the order below.

Note: Open the stopcock prior to packing the column, especially before adding solvent (7.7.4). This procedure minimizes back-pressure problems that disrupt the packing during solvent addition.

7.7.3.1 Add approximately 1 cm of sodium sulfate (5.1.3) to column (the sodium sulfate helps prevent clogging of the column frit by silica fines).

7.7.3.2 Add 3.0 g of 2-percent deactivated silica gel. Assist the packing step by tapping the column above the sorbent layer.

7.7.3.3 Overlay with 5.0 g of 8.5-percent deactivated alumina. Tap the column above the sorbent layer to facilitate packing.

7.7.3.1 Add approximately 1 cm of sodium sulfate to the top of the packing.

7.7.4 Immediately add 40 mL hexane to the column using the solvent dispenser.

Note: Carefully add all solvents down the side of the column wall so as not to disturb the packing.

7.7.5 Attach ball joint to column and apply sufficient nitrogen gas pressure to pass the hexane rinse though the column in about 5 minutes. This helps drive out air and pack the sorbent. Take the solvent layer just into the top sodium sulfate layer; close stopcock.

Caution: At no time after wetting the column packing should the solvent level fall below the top sodium sulfate layer and into the sorbents. If it does so prior to the addition of the sample extract (7.7.9), discard the column packing and repack with new deactivated sorbents.

7.7.6 Add another 10 mL hexane. *Option: If 30 mL of hexane is added instead of 10 mL here, the packed columns can sit unused, with stopcock closed and ball joint attached, for up to 4 hours.*

7.7.7 Pass through the hexane final prerinse at a flow rate amenable to analyst needs (for example, 2 to 5 mL/min) based on packing, prerinsing, and running of simultaneous columns. When approximately 2 to 3 mL of hexane prerinse remain, stop nitrogen pressure, and maintain solvent flow comparable to gravity flow (1 mL/min) until the hexane goes just into the top sodium sulfate layer; close stopcock.

7.7.8 Position a 40-mL K-D receiver tube labeled "fraction 1" (F1) at the column outlet.

7.7.9   Carefully add the sample extract (7.6.4) to the column head using a 22.9-cm Pasteur pipet. Position the pipet just above the top of the sodium sulfate layer and introduce the extract onto the sodium sulfate. Do not disturb the packing.

Note: At the time of sample addition, the sample must be in a completely nonpolar solvent (for example, hexane) and at a volume of 0.5 mL (minimum) to 1.5 mL (maximum). The presence of residual dichloromethane or other "polar" solvent will produce undesirable and irreproducible compound separations.

7.7.10 Open stopcock and allow the sample to drop just into the top sodium sulfate layer; close stopcock.

Note: With GPC cleanup, the extracts are generally clean enough that application of nitrogen pressure during this and subsequent steps usually is not necessary. However, some sediment extracts might require application of slight nitrogen pressure to maintain adequate solvent flow; only use sufficient pressure to achieve previously unobstructed gravity-like flow rates (1 mL/min for hexane).

7.7.11 Rinse the sample tube with 1 mL hexane and carefully pipet the rinse to the column. Open stopcock and allow the rinse to drop just into the top sodium sulfate layer; close stopcock.

7.7.12 Repeat step 7.7.11. The extract and two 1-mL rinses of the sample tube are now loaded onto the column.

7.7.13 Carefully add 27 mL of hexane down the inside wall of the column (do not disturb the packing), cap the ball joint, open the stopcock, and collect solvent into the fraction 1 receiver tube until the hexane just reaches the top sodium sulfate layer; close stopcock. The total volume of F1 is 30 mL.

7.7.14 Replace the F1 receiver with another 40-mL K-D receiver tube labeled "fraction 2" (F2).

7.7.15 Carefully add 35 mL of the 5-percent acetone and 95-percent hexane mixture (see note under 5.7.4), cap the ball joint, open the stopcock, and collect the solvent into the fraction 2 receiver tube until the solvent just reaches the top of the sodium sulfate layer; close stopcock. The total volume of F2 is 35 mL.

7.7.16 Cap and store F1 and F2 at 4°C until step 7.8.

7.7.17 Remove remaining solvent from used columns using 35 kPa nitrogen pressure; the dried packing is easily discharged from the column and discarded.

7.8 Fraction concentration

7.8.1   Add one to two small boiling chips to F2, attach a 3-ball micro-Snyder column to the top of the K-D receiver tube, place tube in an 80°C water bath, and reduce the solvent volume to no less than 1 mL or until distillation slows dramatically (typically at 3- to 6-mL volume). Remove tube from bath and cool.

7.8.2   Raise water bath to 85 to 87°C. Add one small boiling chip to the F2 tube and reduce the solvent volume to no less than 1 mL, or until solvent evaporation dramatically decreases. Remove the tube from the bath and cool.

7.8.3   Further reduce the fraction to 0.5 mL using a gentle stream of nitrogen (4.3.4). Record the final extract volume (V_E) of the fraction.

7.8.4   Carefully transfer the fraction to a crimp-cap vial (5.8.1) using a Pasteur pipet.

7.8.5   Add 10 µL of OCIIS (5.8.2) to the fraction in the crimp-cap vial using a syringe. Cap the vial and store at 4°C until GC/ECD analysis (see section 8).

Note: Exactly match the lot number or NWQL standard solution number of the OCIIS solution that was added to the calibration standard under section 5.10.

7.8.6   Repeat steps 7.8.2 through 7.8.5 for the F1 sample (which requires the higher water bath temperature).

8.   Gas chromatography/electron-capture detection analysis

8.1   Analyze the sample extracts by gas chromatography with electron-capture detection (GC/ECD) using a dual capillary-column system (4.9.1) equipped with an autosampler, one split/splitless injection port (operated in the splitless mode), a 5-m section of uncoated, deactivated guard column (5.9.3), a Y-type column connector (5.9.2) to connect the guard column to the primary (5.9.1.1) and secondary (5.9.1.2) capillary columns, and two electron-capture detectors. Use a computer system to control the autosampler, GC operational conditions, and to acquire and process responses from the dual detectors. Complete details of GC/ECD operation are beyond the scope of this report. The following procedure outlines the suggested GC conditions and autosequence used in this method. Consult the appropriate instrument manuals for additional details regarding general GC/ECD system operation.

8.2   Suggested GC operational conditions -- Note: Use any operational conditions that provide acceptable levels of compound separation, identification, quantitation, accuracy, and precision.

8.2.1   Injection port temperature: 220°C.

8.2.2   Splitless injection split time: 60 seconds.
Split flow rate: 50 mL/min. Septum purge flow rate: 3 to 5 mL/min.

8.2.3   Sample injection volume: 2 to 4 µL.

8.2.4   Oven temperature program: Initial temperature 50°C (hold for 1 minute).
Ramp 1 -- 15°C/min to 140°C
Ramp 2 -- 1°C/min to 210°C
Ramp 3 -- 4°C/min to 280°C, hold for 10 to 30 minutes to allow for sufficient column bake-out.

8.2.5   Electron-capture detector temperature: 350°C (Hewlett-Packard); 380°C (Perkin-Elmer).

8.2.6   Carrier gas: helium at approximately 23 cm/s linear velocity.

8.2.7   Makeup gas: nitrogen at approximately 40 mL/min flow rate.

8.3   Determine compound retention times: Following GC setup, establish compound retention times using the calibration standard solutions. Figure 3 shows typical separation and peak shape obtained using the GC operating conditions of 8.2 for the individual OC pesticides on the Rtx-5 column; figure 4 shows separation and peak shape on the Rtx-1701 column. Table 4 lists peak identifications and retention times for the method compounds and other selected compounds shown in figures 3 and 4.

Note: Because of differences in GC columns, even from the same manufacturer, and chromatographic conditions between instruments, the elution profiles of the method compounds will vary. Therefore, it is critical to verify instrument-specific compound retention times. Use single-component standards to verify retention times of closely or coeluting compounds. Reverify retention times following any GC maintenance procedures applied to the guard or capillary columns to improve chromatography.

8.4   Coelution problems: Various coelutions were observed using the GC conditions described in 8.2. Table 5 lists those compound coelutions that were most commonly observed. Coelution conditions require special identification (8.5.2) and calibration (9.1.2) considerations.

Note: Improved separations of some compounds were achieved with temperature program modifications, but always at the expense of other method compound separations. Separation performance tests conducted on two other Restek Corporation columns (Rtx-50 and -200) provided acceptable separations of most of the problematic compounds listed in table 5, but exhibited inadequate separations of other important method compounds under the limited temperature programs tested.

30
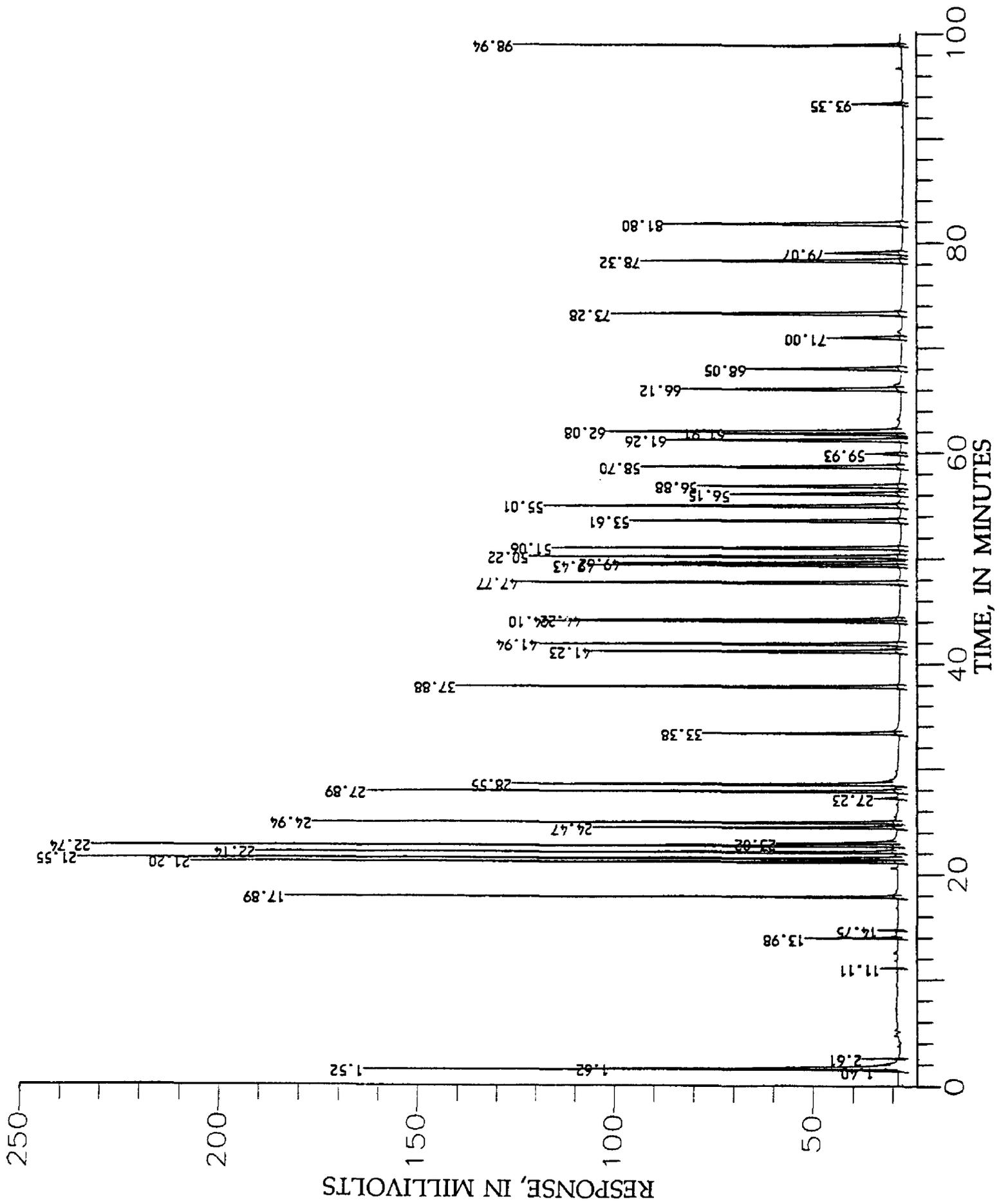
Figure 3.--Gas chromatogram with electron-capture detection of a 50-picograms-per-microliter calibration standard solution of the individual organochlorine pesticides on a Restek Rtx-5 column. Compound identifications are listed in table 4. Chromatographic conditions are given in the text.
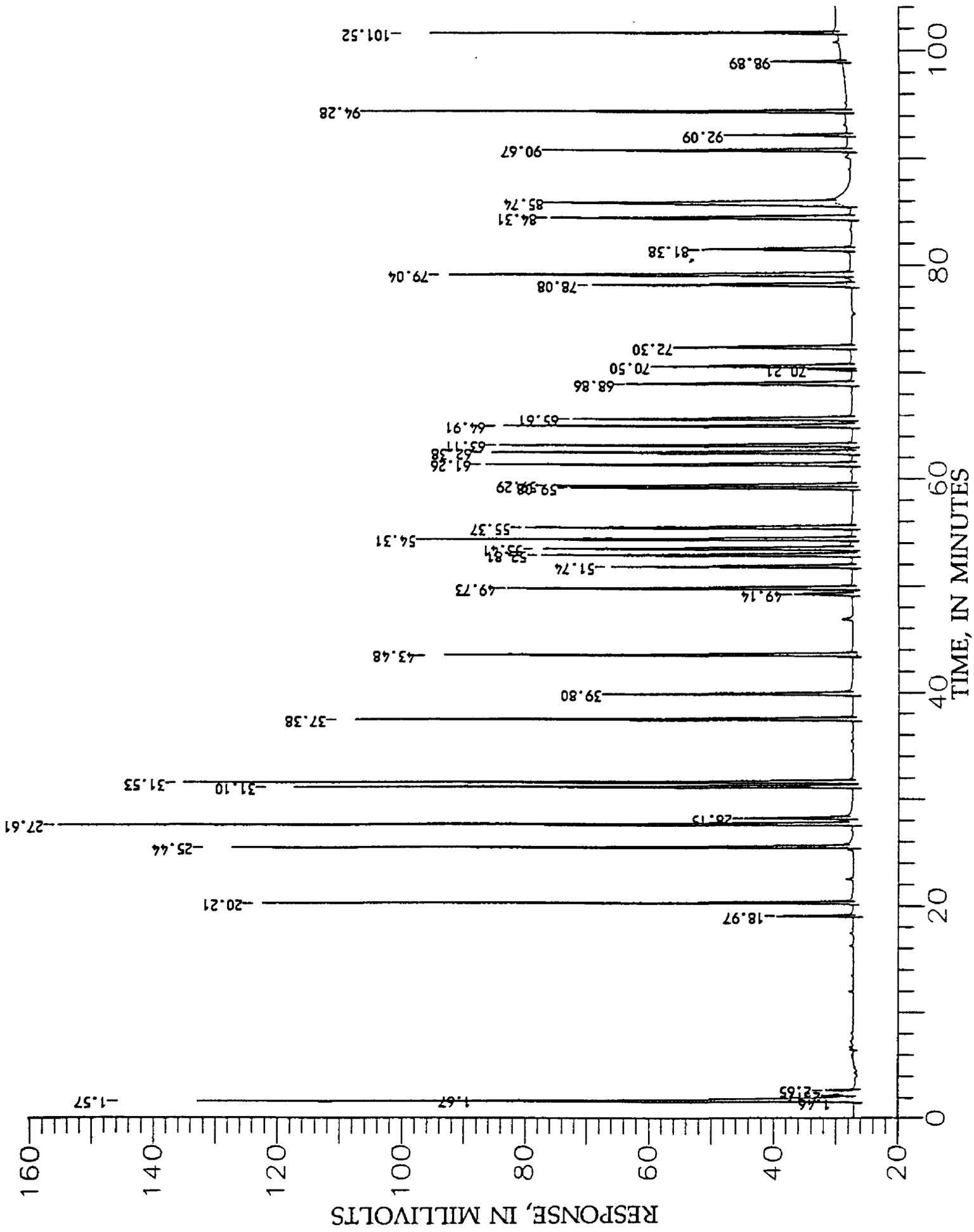
Figure 4.--Gas chromatogram with electron-capture detection of a 50-picograms-per-microliter calibration standard solution of the individual organochlorine pesticides on a Restek Rtx-1701 column. Compound identifications are listed in table 4. Chromatographic conditions are given in the text.

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Table 4.--*Retention times of method compounds and other selected compounds on the Rtx-5 and -1701 columns from figures 3 and 4 example gas chromatograms (listed in Rtx-5 retention time order)*

[±, plus or minus; na, not applicable; ni, not included in standard]

Compound	Retention time (minutes)		Suggested width of retention time window (minute)
	Rtx-5	Rtx-1701	
Chloroneb	13.98	18.97	±0.05
Tetrachloro-m-xylene[a]	17.89	20.21	± .05
alpha-HCH-d$_6$[b]	21.20	31.10	± .05
alpha-HCH	21.55	31.53	± .05
Hexachlorobenzene	22.14	25.44	± .05
Pentachloroanisole	22.74	27.61	± .05
3,5-Dichlorobiphenyl[b]	23.02	28.15	± .05
beta-HCH	24.47	51.74	± .05
gamma-HCH (lindane)	24.94	37.38	± .05
delta-HCH[c]	27.89	54.31	na
Chlorothalonil[c]	28.55	49.14	na
Heptachlor	33.38	39.80	± .07
Aldrin	37.88	43.48	± .07
DCPA	41.23	53.41	± .07
Isodrin	41.94	49.73	± .07
Heptachlor epoxide	[d] 44.10	55.37	± .07
Oxychlordane	[d] 44.22	52.81	± .07
trans-Chlordane	47.77	61.26	± .07
o,p'-DDE	[d] 49.43	[d] 59.08	± .07
Endosulfan I	[d] 49.62	[d] 59.29	± .07
cis-Chlordane	50.22	62.38	± .07
trans-Nonachlor	51.06	63.11	± .07
Dieldrin	53.61	65.61	± .07
p,p'-DDE	55.01	64.91	± .07
o,p'-DDD	56.15	[d] 70.50	± .07
Endrin	56.88	68.86	± .07
Endosulfan II[c]	58.70	78.08	na
Perthane[c]	59.93	[d] 70.21	na
cis-Nonachlor	61.26	[d] 79.04	± .07
p,p'-DDD	[d] 61.91	[d] 79.04	± .07
o,p'-DDT	[d] 62.08	72.30	± .07
Endrin aldehyde[c]	[d] 62.08	[d] 85.74	na
Endosulfan sulfate[c]	66.12	90.67	na
p,p'-DDT	68.05	81.38	± .07

Table 4.--*Retention times of method compounds and other selected compounds on the Rtx-5 and -1701 columns from figures 3 and 4 example gas chromatograms*--Continued

| Compound | Retention time (minutes) | | Suggested width of retention time window (minute) |
	Rtx-5	Rtx-1701	
o,p'-Methoxychlor	71.00	[d] 84.31	± 0.07
Endrin ketone[c]	73.28	94.28	na
PCB-204[b]	78.32	[d] 84.31	± .07
p,p'-Methoxychlor	79.07	92.09	± .07
Mirex	81.80	[d] 85.74	± .07
cis-Permethrin	93.35	98.89	± .1
trans-Permethrin	ni	ni	± .1
Decachlorobiphenyl[a]	98.94	101.52	± .1

[a]Organochlorine internal injection standard compound.

[b]Surrogate compound.

[c]Compound included in the calibration standard, but not included as a final method compound because of inadequate method performance.

[d]Compound largely or completely coelutes with another compound on this column.

Table 5.--*Compound coelutions commonly observed on the gas chromatographic columns used in this method[a]*

Column Rtx-5	Column Rtx-1701
Heptachlor epoxide and oxychlordane	Oxychlordane and DCPA
o,p'-DDE and endosulfan I	*o,p'*-DDE and endosulfan I
o,p'-DDT, *p,p'*-DDD, and endrin aldehyde[b]	*cis*-Nonachlor and *p,p'*-DDD
	o,p'-Methoxychlor and PCB-204[c]

[a]Additional coelutions were occasionally observed (for example, see figures 3 and 4, and table 4).

[b]Endrin aldehyde is a breakdown component of endrin that was included in the calibration standards, but is not a method compound because of poor method performance.

[c]PCB-204 is a surrogate compound.

8.5   Retention time window/compound identification:

8.5.1   A compound is positively identified if it is found within the expected retention time window on both columns and in similar amounts (see 8.5.2). The size of the retention time window is compound dependent. For single component compounds and selected congener peaks from the multicomponent compounds (PCBs and toxaphene, see 9.2.1), set the center of the retention time window using the average of at least three retention time determinations from the initial calibration of a GC sequence (see below). Suggested widths of the retention time windows are listed in table 4. A ±0.1-minute width is recommended for the selected congener peaks used to quantitate PCBs and toxaphene. Alternatively, window widths can be set at plus or minus three times the standard deviation of the average retention time computed from injections of the calibration standard solutions.

8.5.2   Detection of a compound in similar amounts--typically within 30-percent relative percent difference (RPD)--on both columns helps confirm compound identification. Compound coelutions, and, especially, sediment-matrix-specific chromatographic interference problems, are commonly observed in this method, often resulting in RPDs well above 30 percent. Under these conditions, an analyst's judgment is required for compound identification. When applicable, consider the presence of other "family" compounds in the sample to assist in compound identification. (For example, if considering *trans*-chlordane, then other chlordane components should be detected in the sample.) Compounds that show coelution with another method compound (or known nonmethod compound or recognized interferent) on one column, must be quantified on the other column where no coelution problem occurs. The compound still must be found within the expected retention time window on both columns for positive identification.

8.6   GC autosequence: Table 6 lists the recommended sequence for an automated analysis. *Note: Include the applicable multicomponent standard for a F1 or F2 analysis.*

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Table 6.--*Suggested gas chromatography/electron-capture detection autosequence*

[pg/µL, picogram per microliter; F1, fraction 1; F2, fraction 2]

Standard or sample type
Hexane gas chromatograph injection blank
Performance evaluation mix (PEM) (5.10.2.1)
Organochlorine pesticide calibration standard solutions at 5, 10, 20, 50, 100, and 200 pg/µL or other appropriate concentration (5.10.1.1).
Multicomponent calibration standard solutions--polychlorinated biphenyls (F1) or toxaphene (F2) (5.10.1.2 or 5.10.1.3).
Third-party check solution (5.10.2.3)
Reagent lab blank (7.2.2.1)
Reagent organochlorine spike sample (7.2.2.2)
Standard reference material sample (7.2.2.3)
Two field samples
Continuing calibration verification (CCV) standard solution (5.10.2.2)
PEM
Five field samples
CCV
PEM
Five field samples
CCV
PEM

9. Gas chromatography/electron-capture detection compound calibration

The GC/ECD is calibrated (and compounds subsequently quantitated, see section 10) using results obtained on both capillary columns.

9.1 Multipoint external standard calibration for single component compounds. *Option: The internal standard method of calibration and compound quantitation may be used by selecting either one of the OCIIS compounds, tetrachloro-m-xylene or decachlorobiphenyl, provided that there are no chromatographic interferences with these compounds in both the standard solutions and samples. Details regarding internal standard quantitation are not presented here but are provided in McNair and Bonelli (1969, p. 150) and U.S. Environmental Protection Agency (1990b). In the external standard calibration method described below, the OCIIS compounds are used as retention time markers to assist in compound identification.*

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9.1.1   For individual OC pesticides, calibration is achieved using multipoint curves generated from analysis of the 5- to 200-pg/μL (or other) calibration standard solutions (5.10.1.1). Plot the GC/ECD peak area for the compound (A_c) in relation to the mass (in picograms) of the compound for each of the 5- to 200-pg/μL calibration standards injected. Calculate a calibration curve for this plot using the simple linear regression model {of the form $Y = m \times X + b$; where $X = (C_c \times V_1)$}

$$A_c = m \times (C_c \times V_1) + b \tag{3}$$

where m =   compound-specific slope, in area per picogram;

C_c =   concentration of the compound in the standard solutions, in picograms per microliter (5.10.1.1);

V_1 =   volume of calibration standard solutions injected into GC/ECD, in microliters (8.2.3); and

b =   compound-specific y-intercept, in area.

Note: Other regression models may be used as appropriate.

9.1.2   For compounds that may exhibit coelutions on both analytical columns (for example, *p,p'*-DDD), calibrate by using one or more separate standard solutions that contain only one of the coeluting compounds. For example, use separate standard solutions that contain *p,p'*-DDD but not coeluting *o,p'*-DDT and endrin aldehyde (Rtx-5 column), and not coeluting *cis*-nonachlor (Rtx-1701). Calibrate using the separate standard solutions as described in 9.1.1. Identification and quantification of compounds that coelute on both columns require careful consideration by the analyst. For example, *p,p'*-DDD can be quantified on the Rtx-1701 column if there are no other chlordane components present in the sample (thus suggesting no coeluting *cis*-nonachlor). In most cases, the compound that coelutes on both columns will need to be reported as either an upper-limit value, as a raised reporting-limit value, or not reported because of coeluting interference.

9.2   External standard calibration for PCBs and toxaphene.

9.2.1   For PCBs and toxaphene, compute an overall response factor by summing the peak areas for 10 to 15 (or more) representative peaks and dividing by the total concentration of the PCB or toxaphene standard solution. Representative peaks are selected on the basis of adequate peak intensity and separation from other congener, method compound, and interferent peaks (see sections 9.2.2 and 9.2.3). For PCBs, a 1:1:1 mixture of Aroclor 1242, 1254, and 1260 at 200 ng/μL each (or 600 pg/μL total PCBs) typically was used as the calibration standard solution (5.10.1.2). Calculate the response factor using

$$RF = \frac{\text{Sum of select peak areas in PCB or toxaphene standard}}{C_m \times V_1} \quad (4)$$

where RF = response factor, in area per picogram;

C_m = total PCB (5.10.1.2) or toxaphene (5.10.1.3) concentration in standard solution, in picograms per microliter; and

V_1 = volume of standard solution injected into GC/ECD, in microliters (8.2.3).

When multilevel calibration standard solutions are used for PCBs and toxaphene, compute an average response factor if the response-factor values over the working range exhibit a relative standard deviation of less than 30 percent. Alternatively, use the calibration standard solution concentration closest to the observed sample amount.

9.2.2 PCB peak selection: Carefully compare the PCB chromatographic profiles of the calibration standard solutions and field samples, and select peaks for the determination of total PCBs that exhibit minimal interference problems in both the standard and samples. This comparison may result in the selection of different PCB peaks for different field samples, depending on matrix-specific interference or other chromatographic separation problems. The same peaks must be selected for calculating the total PCB response factor (equation 4) that are selected for quantitation of total PCBs in a given field sample (equation 7).

9.2.2.1 Selection of PCB peaks on the Rtx-5 column: Figure 5 shows an example gas chromatogram of the mixed 1:1:1 Aroclor 1242, 1254, and 1260 calibration standard solution on the Rtx-5 column using the same gas chromatographic system and conditions used to produce the Rtx-5 chromatogram of the individual OC pesticide calibration standard solution shown in figure 3. Suggested peaks to select from the Rtx-5 column for computing a PCB response factor (equation 4) and for subsequent quantitation of total PCBs in a sample (equation 7) are listed in table 7. Suggested peaks are grouped into primary (A) or secondary (B) categories for peak selection on the basis of chromatographic considerations, including coelution with other PCB peaks or other fraction 1 method compounds (see table 3). Tentative identification of congeners present in the suggested peaks are listed in table 7 and are based on published chromatographic characterizations of these Aroclor standard solutions on similar GC columns coated with a 5-percent diphenyl- and 95-percent dimethyl-polysiloxane stationary phase (Mullin and others, 1984; Eganhouse and others, 1989; Schulz and others, 1989). The percentage of each congener present in Aroclor 1242, 1254, and 1260, as determined by Schulz and others (1989), also is listed in table 7.
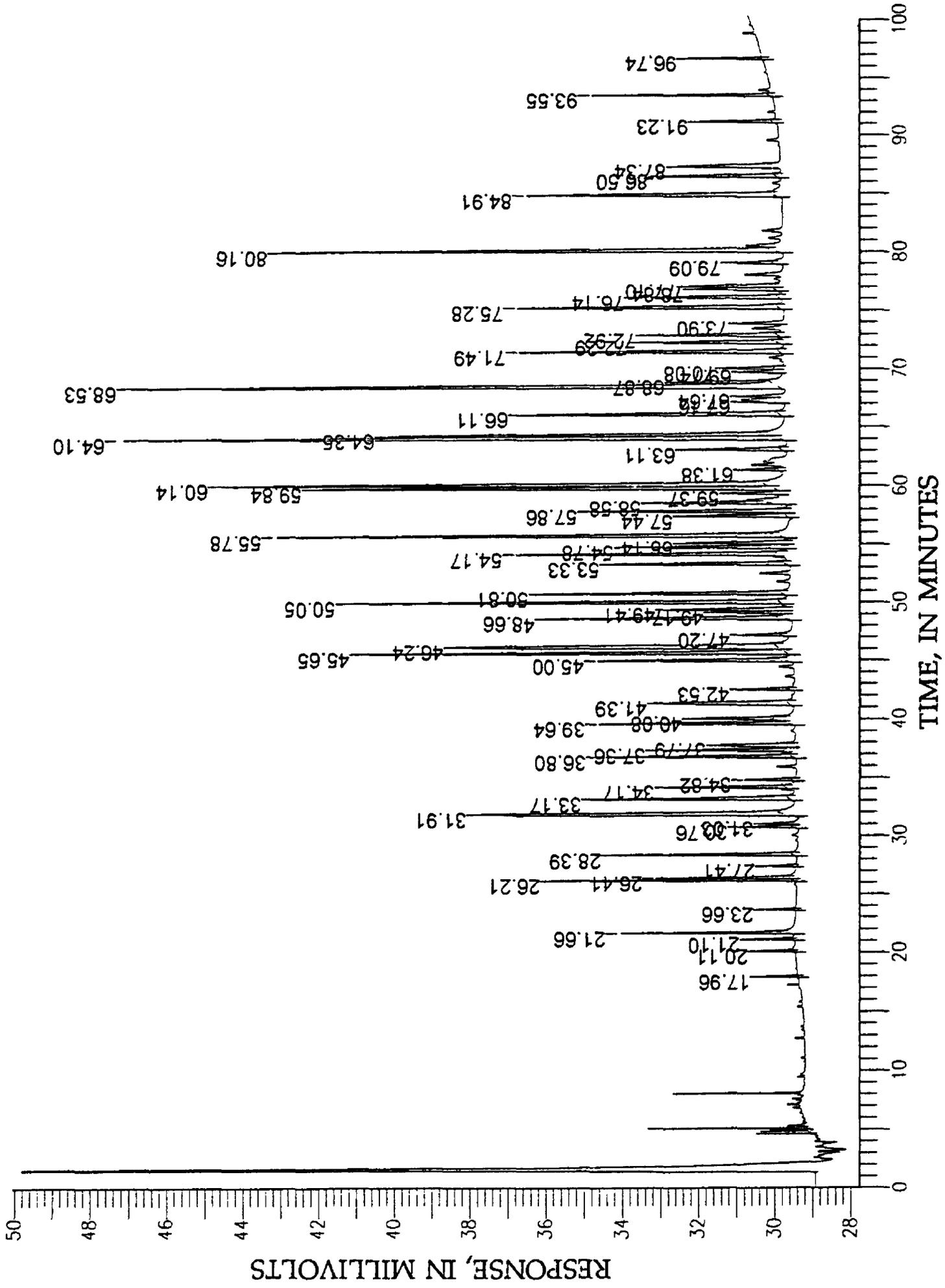
Figure 5.--Gas chromatogram with electron-capture detection on a Restek Rtx-5 column of a mixed Aroclor 1242, 1254, and 1260 calibration standard solution containing 100 picograms per microliter per Aroclor. Suggested peaks to select for PCB calibration and quantitation are listed in table 7. Chromatographic conditions are given in the text.

Table 7.--*Suggested peaks for calibration and quantitation of total polychlorinated biphenyls on the Rtx-5 column based on the figure 5 example gas chromatogram of a mixed Aroclor 1242, 1254, and 1260 calibration standard solution*
(Peaks listed in order of elution on Rtx-5 column)

[--, not detected in Aroclor at greater than 0.05 percent]

Peak selection category[a]	Peak retention time on Rtx-5 column from figure 5 (minutes)	Tentative congener identification[b]	Percentage of congener in Aroclor standard on a weight per weight basis[c]		
			Aroclor 1242 (percent)	Aroclor 1254 (percent)	Aroclor 1260 (percent)
A	21.66	5	0.06	--	--
		8	7.65	--	--
B	26.21	18	6.28	0.41	--
B	26.41	15	1.51	--	--
		17	2.88	0.19	--
A	28.39	16	2.01	--	--
		32	0.88	--	--
A	36.80	52	4.04	5.18	0.56
A	39.64	44	3.20	2.03	--
A	40.08	37	0.27	--	--
		42	0.83	0.23	--
		59	0.34	--	--
A	45.00	74	2.17	0.78	--
A	45.65	70	3.89	3.21	0.09
A	50.05	90	0.32	0.93	0.56
		101	1.33	7.94	5.02
A	50.81	99	0.86	3.60	0.11
A	53.33	97	0.65	2.55	0.23
A	54.17	87	0.77	3.78	0.77
		115	--	0.30	0.05
A	55.78	77	0.45	--	--
		110	1.53	5.85	1.90
A	59.84	123	--	0.81	--
		149	0.63	2.21	7.83
A	60.14	118	1.62	6.39	0.57
A	66.11	141	--	1.04	2.56
		179	--	0.21	1.79
A	68.53	138	0.54	3.20	6.13
		160	--	--	0.05
A	71.49	187	--	0.32	3.97
A	72.29	183	--	0.17	1.76
A	72.92	128	--	2.07	1.06
A	75.28	174	--	0.34	3.85

Table 7.--*Suggested peaks for calibration and quantitation of total polychlorinated biphenyls on the Rtx-5 column based on the figure 5 example gas chromatogram of a mixed Aroclor 1242, 1254, and 1260 calibration standard solution*--Continued

Peak selection category[a]	Peak retention time on Rtx-5 column from figure 5 (minutes)	Tentative congener identification[b]	Percentage of congener in Aroclor standard on a weight per weight basis[c]		
			Aroclor 1242 (percent)	Aroclor 1254 (percent)	Aroclor 1260 (percent)
A	76.14	177	--	0.21	2.21
A	80.16	180	0.06	0.38	7.12
A	84.91	170	0.11	0.31	3.91
		190	--	0.08	0.79
A	86.50	199	--	--	1.31
A	93.55	194	--	--	1.30
		Total	44.88	54.72	55.50

[a]Select primary (A) peaks before using secondary (B) peaks.

[b]Congener identification numbers from Ballschmiter and Zell (1980). Tentative congener identities in peaks are based on characterizations of Aroclor standard solutions by Mullin and others (1984), Eganhouse and others (1989), and Schulz and others (1989).

[c]Composition of congeners in Aroclor standard solutions as determined by Schulz and others (1989).

9.2.2.1 Selection of PCB peaks on the Rtx-1701 column: Similarly, figure 6 shows an example gas chromatogram of the PCB calibration solution on the Rtx-1701 column. Suggested primary (A) and secondary (B) PCB peaks to select from the Rtx-1701 chromatogram are noted directly in figure 6. Unlike the Rtx-5 column, congener characterization studies of PCB peaks chromatographed on a 14-percent cyanopropylphenyl- and 86-percent dimethyl-polysiloxane stationary phase (Rtx-1701 type) have not been published.
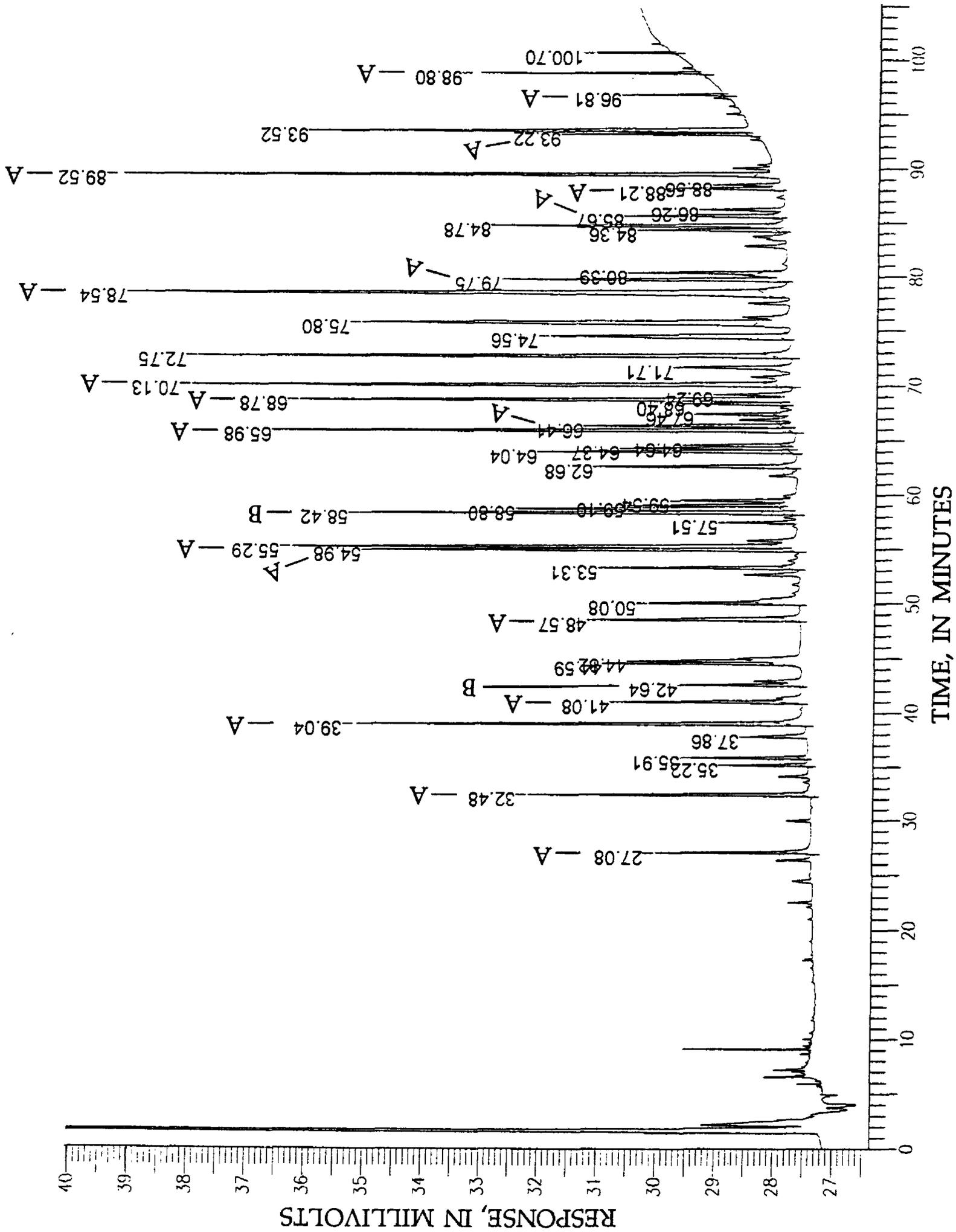
Figure 6.--Gas chromatogram with electron-capture detection on a Restek Rtx-1701 column of a mixed Aroclor 1242, 1254, and 1260 calibration standard solution containing 100 picograms per microliter per Aroclor. Suggested primary (A) and secondary (B) peaks to select for PCB calibration and quantitation are shown. Chromatographic conditions are given in the text.

9.2.3   Toxaphene peak selection: Select peaks for toxaphene using the approach described for PCBs (9.2.2). Toxaphene peak selection is left to an analyst's discretion after very careful comparison of sample and toxaphene standard chromatographic patterns.

Note: GC/ECD analysis of toxaphene in bed sediments typically is much more complicated than the analysis of PCBs. Toxaphene reportedly contains hundreds of compounds (Jansson and Wideqvist, 1983; Saleh, 1991), and, unlike PCBs, has not been well characterized (Swackhamer and others, 1987; Bidleman and others, 1993). In this method, toxaphene is present predominantly in the fraction 2 extract (see table 3), and coelution of toxaphene congeners with other method compounds will occur. Avoid selecting toxaphene peaks that coelute with other commonly observed method compounds (especially p,p'-DDT, p,p'-DDD, dieldrin, cis- and trans-chlordane and cis- and trans-nonachlor). Toxaphene also undergoes considerable environmental weathering, primarily because of differential environmental partitioning as a result of the widely varying physical/chemical properties of its components. Additionally, many toxaphene components are susceptible to reductive dechlorination reactions in anoxic bed sediments. These environmental weathering processes (especially the dechlorination process) often produce an enrichment in earlier eluting components, resulting in chromatographic patterns that are not characteristic of the chromatogram obtained with the technical toxaphene calibration standard solution (Williams and Bidleman, 1978; Harder and others, 1983). In this method, determination of toxaphene relies on visual pattern recognition of toxaphene in a sample chromatogram relative to the toxaphene standard solution. Therefore, an analyst may not readily recognize heavily altered toxaphene in a field sample by GC/ECD. The presence of toxaphene can be confirmed using GC with electron-capture negative ionization mass spectrometry (see for example, Swackhamer and others, 1987; Patton and others, 1989; Muir and others, 1992).

10.   Calculation of results

10.1 Calculate the dry weight of sediment extracted, in grams (W_s):

$$W_s = W_w \times f_d \tag{5}$$

where W_w =   wet weight of sediment, in grams (7.1.6); and
             f_d =   dry-weight fraction of sediment (7.1.5).

10.2 Calculate the concentration of compounds in the sample.

10.2.1 For the individual OC compounds:

10.2.1.1 Use the compound-specific regression parameters *m* and *b* (equation 3) from the calibration curve to calculate the raw amount (*RA*, in picograms per microliter) of compound in the analyzed sample extract using

$$RA = \frac{(A_S - b)}{m \times V_2} \qquad (6)$$

where A_S =   the peak area of the identified compound in the sample extract; and

V_2 =   volume of extract injected into GC/ECD, in microliters (8.2.3).

10.2.2 For PCBs and toxaphene:

    10.2.2.1 Sum the peak areas for all identified PCB or toxaphene congeners in the sample that match the retention times of those peaks selected for the PCB or toxaphene calibration standard solutions (9.2.1-9.2.3). Calculate the raw amount (RA_m, in picograms per microliter) of PCBs or toxaphene in the analyzed sample extract using

$$RA_m = \frac{\text{Sum of select congener peak areas in sample}}{RF \times V_2} \qquad (7)$$

where RF =   the PCB or toxaphene response factor, in area per picogram (calculated from equation 4); and

V_2 =   volume of extract injected into GC/ECD, in microliters (8.2.3).

    10.2.3 Calculate the concentration (C_S) of the identified compound in the sample, in micrograms per kilogram of dry-weight sediment, using

$$C_S = \frac{RA \times V_E \times (W_1/W_2)}{W_S} \qquad (8)$$

where C_S =   concentration of compound in sample, in micrograms per kilogram (equivalent to nanograms per gram);

RA =   raw amount of compound, in nanograms per milliliter (equivalent to picograms per microliter) (calculated from equation 6);

V_E =   volume of sample extract just prior to GC/ECD, in milliliters (7.8.3);

W_1 =   weight of sample extract before GPC, in grams (calculated from equation 1);

W_2 =   weight of sample extract processed through the GPC, in grams (calculated from equation 2); and

W_S =   dry weight of sample extracted, in grams (calculated from equation 5).

Note: For PCBs and toxaphene substitute RA_m from equation 7 for RA in equation 8.

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10.3 Calculate the percent recovery of the surrogate compounds in each sample using

$$R_a = \left[\frac{C_S}{(C_a \times V_a)/W_S}\right] \times 100 \qquad (9)$$

where R_a = recovery of surrogate in sample, in percent;

C_S = determined concentration of surrogate in sample, in nanograms per gram (equivalent to micrograms per kilogram) (calculated from equation 8);

C_a = concentration of compound in the surrogate solution added to the sample, in nanograms per microliter (5.2.4);

V_a = volume of surrogate solution added to the sample, in microliters (7.2.5); and

W_S = dry weight of sample, in grams (calculated from equation 5).

10.4 Calculate the percent recovery of compounds in reagent OC spike sample using

$$R_b = \left[\frac{C_S}{(C_b \times V_b)/W_S}\right] \times 100 \qquad (10)$$

where R_b = recovery of spiked compound in the reagent OC spike sample, in percent;

C_S = determined concentration of compound in reagent OC spike sample, in nanograms per gram (calculated from equation 8);

C_b = concentration of compound in OC spike solution added to sample, in nanograms per microliter (5.2.5);

V_b = volume of OC spike solution added to the sample, in microliters (7.2.2.2); and

W_S = dry weight of sample, in grams. *Note: The actual (or assumed) sample weight (W_S) of the matrix used for preparing the reagent spike sample must be equivalent in both equations 8 and 10.*

10.5 Calculate the percent recovery of compounds in the SRM sample using

$$R_{SRM} = \left[\frac{C_S}{C_{SRM}}\right] \times 100 \qquad (11)$$

where R_{SRM} = recovery of spiked compound in the SRM sample, in percent;

C_S = determined concentration of compound in the SRM sample, in nanograms per gram (calculated from equation 8); and

C_{SRM} = expected concentration of compound in the SRM sample, in nanograms per gram (5.2.8).

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10.6 Calculate the percent degradation of p,p'-DDT and endrin on the GC/ECD from injections of the PEM (5.10.2.1) using the following equations:

$$\text{percent } p,p'\text{-DDT loss} = \frac{A_{p,p'\text{-DDD}} + A_{p,p'\text{-DDE}}}{A_{p,p'\text{-DDT}} + A_{p,p'\text{-DDD}} + A_{p,p'\text{-DDE}}} \times 100 \qquad (12)$$

$$\text{percent endrin loss} = \frac{A_{\text{endrin aldehyde}} + A_{\text{endrin ketone}}}{A_{\text{endrin}} + A_{\text{endrin aldehyde}} + A_{\text{endrin ketone}}} \times 100 \qquad (13)$$

where A_{compound} = peak area of given compound in the PEM chromatogram.

10.7 Compute the CCV percent difference.

10.7.1 Calculate the raw amount for each compound in the CCV standard solution (RA_{ccv}) using equation 6.

10.7.2 Calculate the percent difference between the determined and expected CCV concentrations using

$$\text{CCV percent difference} = \left[\frac{RA_{ccv} - C_e}{C_e}\right] \times 100 \qquad (14)$$

where RA_{ccv} = calculated raw amount of compound in CCV standard solution, in picograms per microliter (from 10.7.1); and
C_e = expected concentration of compound in CCV standard solution, in picograms per microliter (5.10.2.2).

10.8 Calculate the percent moisture of the uncentrifuged sediment (7.1.4) using

$$\text{percent moisture in uncentrifuged sediment} = \left[\frac{(W_a - W_b) + (W_b \times f_w)}{W_a}\right] \times 100 \qquad (15)$$

where W_a = weight of sample-water mixture prior to centrifugation, in grams (from 7.1.4);
W_b = weight of centrifuged sample-water mixture after decanting water, in grams (from 7.1.4); and
f_w = wet-weight fraction of sediment (7.1.5).

Note: The percent moisture of the uncentrifuged sediment is not required for calculation of the compound concentrations in micrograms per kilogram dry-weight

sediment. This percent moisture value is being reported by request so that, if necessary, users can calculate the compound concentrations in micrograms per kilogram wet-weight sediment to allow comparison with historical data reported on a wet-weight sediment basis. The percent moisture of the uncentrifuged sediment calculated by equation 15 does not include the amount of water decanted from the sediment sample prior to sample freezing for storage (6.3). Concentrations calculated on a dry-weight basis are much more accurate than those calculated on a wet-weight basis because of the highly variable amounts of water used to process the field-sediment samples.

11. Gas chromatography/electron-capture detection performance

11.1 For GC/ECD instrumental analysis, gas chromatograph performance is indicated by peak shape, the efficiency of separation for closely eluting compound pairs, and by the variation in detector response over time for compounds from calibration and CCV standard solutions. Daily assessments of these characteristics are made relative to the performance obtained with new capillary columns and GC inlet liner, and by using freshly prepared standard calibration solutions. When either peak shape, separation efficiency, or response fail to meet performance criteria, instrument maintenance is required. Routine maintenance includes replacement of the injection port liner (5.9.4) and septum. If this does not result in acceptable performance, short lengths (0.3 m) of the guard column (5.9.3) should be removed first to try to restore chromatographic performance. Continued poor chromatographic performance may require replacement of the entire guard column and Y-connector (5.9.2), and removal of short lengths (0.3 to 1 m) of the capillary columns (5.9.1), or complete replacement of the capillary columns. Response factor drops or instability also can be caused by instability in electron-capture detector performance. If the aforementioned steps do not improve response factors, then electron-capture detector maintenance may be required.

11.2 GC/ECD performance criteria

11.2.1 The correlation coefficient (r^2) for the calibration curve regression (equation 3) should be equal to or greater than 0.995. If the r^2 is less than 0.995, the curve may still be used provided that the criteria in section 11.2.2 are met for all calibration levels.

11.2.2 Reprocess all calibration standard solutions against the initial calibration curve (9.1.1). Resultant determined concentrations must be within ±20 percent of the expected concentration for each individual OC pesticide and surrogate on at least one column before proceeding with sample quantitation.

11.2.3 The determined concentration for the third-party check (TPC) standard(s) (5.10.2.3) should be within ±30 percent of the expected concentration.

11.2.4 The performance evaluation mix (5.10.2.1) is injected near the beginning of a GC/ECD sequence and following every five set samples (table 6)

to monitor the degradation of labile compounds (especially p,p'-DDT and endrin) in the GC injection system. The calculated percent loss of p,p'-DDT (equation 12) and endrin (equation 13) should not exceed 30 percent for each compound on more than one column. If losses exceed 30 percent, a dirty injection port liner is usually the cause, and the liner should be immediately replaced with a clean, deactivated liner (5.9.4), followed by other GC maintenance (11.1) as required to reduce the losses to acceptable levels.

       11.2.5 Continuing calibration verification standard solutions are injected following every five set samples throughout the GC sequence (table 6). The calculated CCV percent difference (equation 14) must be within ±30 percent for each compound on at least one column.

       Note: The use of internal standard quantitation methods may help reduce the level of GC/ECD performance variation to be within the aforementioned acceptance criteria.

       11.3 Other GC/ECD performance requirements -- Dilute sample concentrations that exceed the high concentration calibration standard to within the calibration range.

12. Reporting of results

       12.1 *Column-dependent quantitation* -- The quantitative value that is reported is column dependent. Report the lower concentration produced by the two GC columns unless it has been demonstrated by the calibration, CCV, TPC, or PEM standards that one of the columns is causing a method compound to degrade or otherwise produce errant results. Column-specific quantitation also will be necessary for those compounds that exhibit coelution or other apparent interference on one GC column (see 8.5.2).

       12.2 *Reporting units* -- Compound concentrations in field samples are reported in micrograms per kilogram dry-weight sediment (equation 8). For sample concentrations less than 10 µg/kg, report two significant figures; for concentrations above 10 µg/kg, report three significant figures. Surrogate data for each sample type are reported in percent recovered (equation 9). Data for the reagent spike and SRM samples are reported in percent recovered (equations 10 and 11). Compounds quantified in the reagent blank sample are reported in micrograms per kilogram, using an actual or assumed 25-g dry-sample weight (equation 8).

       12.3 *Reporting limits* -- Estimates of method detection limits (MDLs) using the procedures outlined by the U.S. Environmental Protection Agency (1992b) have not been fully completed for this method (see following Method Performance section). Interim reporting limits for this method are listed in table 8. These reporting limits were chosen in part because of the following: (1) the partial MDL data collected using the reagent OC spike sample recovery data (see

Method Performance section); (2) considerations of compound sensitivity relative to typical matrix-derived instrumental noise levels encountered in most sediment samples processed to date with this method; and (3) the susceptibility of selected compounds to degrade in the GC injection system.

Table 8.--*Interim low-end method reporting limits*

[μg/kg, micrograms per kilogram]

Compound	Method reporting limit (μg/kg)
Aldrin	1
cis-Chlordane	1
trans-Chlordane	1
Chloroneb	5
DCPA (Dacthal)	5
o,p'-DDD	1
p,p'-DDD	1
o,p'-DDE	1
p,p'-DDE	1
o,p'-DDT	2
p,p'-DDT	2
Dieldrin	1
Endosulfan I	1
Endrin	2
Heptachlor	1
Heptachlor epoxide	1
Hexachlorobenzene	1
alpha-Hexachlorocyclohexane	1
beta-Hexachlorocyclohexane	1
gamma-Hexachlorocyclohexane	1
Isodrin	1
o,p'-Methoxychlor	5
p,p'-Methoxychlor	5
Mirex	1
cis-Nonachlor	1
trans-Nonachlor	1
Oxychlordane	1
Pentachloroanisole	1
cis-Permethrin	5
trans-Permethrin	5
Polychlorinated biphenyls (total)	50
Toxaphene (technical)	200

METHOD PERFORMANCE

Following development of the original method, a preliminary method performance evaluation was conducted using replicate reagent and matrix spike recovery tests (see Appendix A). Following a change in the adsorption chromatography procedure (see Appendix B), the method was implemented under routine operation at the NWQL on January 7, 1993. Subsequently, selected portions of the method were further modified to improve performance and reliability. The procedure detailed in sections 1 through 12 and the following performance data reflect all method improvements that were completely implemented on May 19, 1993 (beginning with sample set 93139C). These performance data are limited to sample surrogate recovery information, and to results of method quality-control samples (specifically reagent spike, SRM, and duplicate field-sediment samples) that were processed along with field-sediment samples analyzed for the National Water-Quality Assessment program. No additional method performance data, including replicate matrix spike samples, are available. The procedural differences and preliminary performance results obtained with the original method, including recovery results for some matrix-spike samples, are summarized in Appendix A and included as a supplement to the partial performance data obtained for the final method. The methodological changes incorporated from January 7 through May 19, 1993 (sets 93007A through 93139B) and the resultant impacts on data quality are briefly summarized in Appendix B specifically for the Survey's NAWQA program.

Reagent spike recovery results--The average recoveries of method and other individual pesticides from 13 sodium sulfate reagent OC spike (7.2.2.2) samples processed with 13 sets of sediment samples are listed in table 9. These reagent OC spike samples were fortified at 200 ng of each compound per sample or 8 μg/kg, assuming a 25-g sample weight. Estimated MDLs were calculated from the reagent OC spike sample data using the USEPA MDL procedure (U.S. Environmental Protection Agency, 1992b) and also are listed in table 9.

The estimated MDLs in table 9 reflect variation associated with 13 separate reagent OC spike sample preparations and GC/ECD calibrations. These MDLs range from nearly equivalent to approximately four times greater than the interim reporting limits listed in table 8 for most method compounds. However, the estimated MDLs for chloroneb, DCPA, and the methoxychlors and permethrins are slightly lower than the assigned interim reporting levels (<5 μg/kg). These higher interim reporting levels were prescribed primarily because of the poorer ECD sensitivity of these compounds, especially with regard to sediment matrix-related interferences commonly observed in the GC chromatograms, and also because of susceptibility of the methoxychlors to degradation in dirty GC injection systems.

Table 9.--*Mean recovery of method and other individual pesticides from 13 sodium sulfate reagent organochlorine spike samples processed with sets 93139C through 93235A and estimated method detection limits*

[μg/kg, micrograms per kilogram; ni, not in spike solution; --, not determined]

Compound[a]	Mean recovery (percent)	Standard deviation (percent)	Number of observations[b]	Estimated method detection limit[c] (μg/kg)
Aldrin	69	13	13	2.9
cis-Chlordane	ni	--	--	--
trans-Chlordane	79	10	13	2.1
Chloroneb	66	7	13	1.5
Chlorothalonil[d]	43	21	5	--
DCPA	76	11	13	2.3
o,p'-DDD	71	13	13	2.7
p,p'-DDD	74	10	7	2.2
o,p'-DDE	74	14	10	3.1
p,p'-DDE	76	16	13	3.4
o,p'-DDT	78	13	13	2.8
p,p'-DDT	78	11	13	2.4
Dieldrin	89	20	13	4.2
Endosulfan I	63	9	13	2.0
Endosulfan II[d]	35	11	13	--
Endosulfan sulfate[d]	3	3	12	--
Endrin	76	12	13	2.6
Endrin aldehyde[d]	5	1	7	--
Endrin ketone[d]	3	2	12	--
HCB	65	13	13	2.8
alpha-HCH	56	8	13	1.6
beta-HCH	73	9	13	1.9
delta-HCH[d]	42	17	13	--
gamma-HCH	66	9	13	2.0
Heptachlor	48	10	13	2.2
Heptachlor epoxide	72	10	13	2.3
Isodrin	73	14	13	3.0
o,p'-Methoxychlor	72	14	13	3.1
p,p'-Methoxychlor	77	16	13	3.4
Mirex	70	17	13	3.7
cis-Nonachlor	85	12	13	2.6
trans-Nonachlor	80	11	13	2.3
Oxychlordane	72	12	10	2.7
Pentachloroanisole	74	11	13	2.3

Table 9.--*Mean recovery of method and other individual pesticides from 13 sodium sulfate reagent organochlorine spike samples processed with sets 93139C through 93235A and estimated method detection limits*--Continued

Compound[a]	Mean recovery (percent)	Standard deviation (percent)	Number of observations[b]	Estimated method detection limit[c] (μg/kg)
cis-Permethrin	85	14	13	3.0
trans-Permethrin	88	13	13	2.9
Surrogates				
3,5-DCB[e]	60	10	13	2.3
PCB-204[e]	42	7	13	1.5
alpha-HCH-d$_6$[f]	64	9	13	1.9

[a]All compounds were spiked at 200 nanograms per sample or at 8 micrograms per kilogram, assuming a 25-gram sample weight.

[b]Numbers less than 13 resulted from the inability to quantitate the compound in a spike sample because of coelution problems, except for chlorothalonil, which exhibited calibration problems, and endrin ketone and endosulfan sulfate, which exhibited one fractionation problem.

[c]Estimated method detection limits were determined from these reagent organochlorine spike sample results using the U.S. Environmental Protection Agency (1992b) procedure.

[d]Compound included in the individual organochlorine pesticide spike solution (5.2.5), but not included as a final method compound because of inadequate method performance.

[e]Fraction 1 surrogate compound.

[f]Fraction 2 surrogate compound.

According to the U.S. Environmental Protection Agency (1992b) procedure, the fortified concentrations should be no more than five times the estimated MDL; otherwise, an optional iterative procedure should be followed to verify the reasonableness of the MDL estimates. Because the fortified concentration (8 μg/kg) was less than five times the estimated MDLs for many of the pesticides in table 9, these estimated MDLs appear to be appropriate. However, the GC response for this spike level suggests that determining the MDL at lower concentrations might provide lower estimated MDLs for some compounds than those provided in table 9. Therefore, at this time (February 1995), the interim reporting limits listed in table 8 are maintained, since these limits have been used since January 1993. Estimated MDLs for total PCBs and toxaphene have not been determined.

Although the MDL provides a useful reference for the detection of compounds in clean matrices, the MDL does not represent a limiting factor in chemical-noise dominated analyses, like the determination of pesticides in sediment samples by GC/ECD. In this method, matrix-related chemical noise often will result in the inability to detect one or more of the pesticides in a given sample at the MDL.

Table 9 also includes mean recovery data for six compounds that were included in the OC spike mixture, but were deleted as compounds in the final method because of performance-related problems. Likewise, table 10 lists nine compounds that were evaluated during the initial performance tests of the original method (Appendix A) or during early implementation of the method and the reason for their deletion from the final method.

Table 10.--*Compounds tested and the reason for their deletion from this method*

Compound tested	Reason for deletion
Chlorothalonil	Unstable on gas chromatograph (GC). Unable to reliably calibrate on GC.
Endrin aldehyde	Inadequate adsorption chromatography recovery. Unstable on GC.
Endrin ketone	Inadequate adsorption chromatography recovery.
Endosulfan II	Inadequate adsorption chromatography recovery.
Endosulfan sulfate	Inadequate adsorption chromatography recovery.
Hexachlorobutadiene	Unstable on GC. Interference problems on GC.
delta-Hexachlorocyclohexane	May be unstable in solution. May be unstable on GC.
Hexachlorocyclopentadiene	Unstable on GC. Interference problems on GC.
Perthane	Very poor electron-capture detector response.

Average recoveries of method compounds from another 16 sodium sulfate reagent OC spike samples processed with 16 sets of sediment samples are listed in table 11. For these spike samples, new spike and surrogate solutions commercially prepared in hexane were used instead of solutions prepared in methanol for the data listed in table 9, since hexane should be a better solvent for many of the OC pesticides (see 5.2.5 note). The recovery data for these two groups of spike samples were compared using a nonparametric Mann-Whitney rank-sum test and with graphical box plots of the recoveries. For PCB-204 and heptachlor, the mean and median recovery data observed when using the hexane surrogate and spike solutions were higher than those for the methanol solutions, and were statistically different at the 95-percent confidence level ($p < 0.05$).

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Conversely, for *trans*-chlordane, dieldrin, *cis*- and *trans*-nonachlor, pentachloroanisole, and *cis*- and *trans*-permethrin, the mean and median recoveries were significantly lower for spikes using the hexane solution (p<0.5). The other 22 compounds and 2 surrogates were not significantly different at p=0.5. For PCB-204, preparation of the surrogate solution in hexane seems to have improved the recoveries, since this compound was noted to precipitate from methanol solutions upon refrigerated storage. For the other compounds, it is unclear whether the solvent had an effect on the observed recovery differences or whether these differences reflect concentration biases resulting from the preparation of these multicomponent solutions.

Table 11.--*Mean recovery of method pesticides from 16 sodium sulfate reagent organochlorine spike samples processed with sets 93291A through 94.110 and estimated method detection limits*

[μg/kg, micrograms per kilogram]

Compound[a]	Mean recovery (percent)	Standard deviation (percent)	Number of observations[b]	Estimated method detection limit[c] (μg/kg)
Aldrin	66	18	16	3.7
cis-Chlordane	69	9	16	1.9
trans-Chlordane	69	9	16	1.8
Chloroneb	61	15	16	3.1
DCPA	73	9	16	1.8
o,p'-DDD	72	10	16	2.1
p,p'-DDD	72	12	9	2.8
o,p'-DDE	73	14	16	2.8
p,p'-DDE	70	17	16	3.5
o,p'-DDT	70	13	16	2.7
p,p'-DDT	71	9	16	1.8
Dieldrin	65	13	16	2.7
Endosulfan I	54	13	16	2.7
Endrin	75	10	16	2.1
HCB	64	14	16	3.0
α-HCH	57	8	16	1.6
β-HCH	68	8	16	1.6
γ-HCH	63	7	16	1.6
Heptachlor	62	16	16	3.3
Heptachlor epoxide	69	9	16	1.8
Isodrin	65	16	16	3.3
o,p'-Methoxychlor	73	12	16	2.5
p,p'-Methoxychlor	76	11	16	2.2
Mirex	66	16	16	3.4

Table 11.--*Mean recovery of method pesticides from 16 sodium sulfate reagent organochlorine spike samples processed with sets 93291A through 94.110 and estimated method detection limits*--Continued

Compound[a]	Mean recovery (percent)	Standard deviation (percent)	Number of observations[b]	Estimated method detection limit[c] (μg/kg)
cis-Nonachlor	69	10	16	2.2
trans-Nonachlor	69	9	16	1.8
Oxychlordane	71	10	9	2.3
Pentachloroanisole	62	9	16	1.9
cis-Permethrin	72	12	14	2.5
trans-Permethrin	74	14	13	3.0
Surrogates				
3,5-DCB	60	15	16	3.2
PCB-204	77	18	16	3.8
α-HCH-d$_6$	64	11	16	2.3

[a]All compounds were spiked at 200 nanograms per sample or at 8 micrograms per kilogram, assuming a 25-gram sample weight.

[b]Numbers less than 16 resulted from the inability to quantitate the compound in a spike sample because of coelution or other quantitation problems.

[c]Estimated method detection limits were determined from these reagent organochlorine spike sample results using the U.S. Environmental Protection Agency (1992b) procedure.

Surrogate recoveries--Three surrogate compounds are added to all sample types to monitor for methodological errors for an individual sample. The surrogate recoveries are not used to correct concentrations of other method compounds, since the surrogates do not exactly chemically mimic all of the method compounds. The surrogates also were selected to help indicate problems with the adsorption chromatography portion of the method. The fraction 1 surrogates are 3,5-DCB and PCB-204, and the fraction 2 surrogate is α-HCH-d$_6$ (table 3). Surrogate observations that indicate errors in the adsorption chromatography procedure are shown in table 12. Severe matrix effects also may result in erroneous fractionations. As previously noted (7.7), changes in the source or lot of sorbent used will likely result in fractionation differences for the surrogates, as well as the method compounds.

Table 12.--*Surrogate observations that indicate adsorption chromatography errors*

[F1, fraction 1; F2, fraction 2]

Surrogate observation	Possible reason for error
α-HCH-d$_6$ in F1	Not all dichloromethane removed from extract before adsorption chromatography step. Collected more than 30 milliliters of hexane for F1. Used 5-percent acetone in hexane instead of hexane for F1. Incorrect sorbent activation or deactivation.
3,5-DCB and PCB-204 in F2	Collected less than 30 milliliters of hexane for F1. Incorrect sorbent activation or deactivation.
No α-HCH-d$_6$ in F1 or F2	Collected less than 35 milliliters of 5-percent acetone/hexane for F2. Used hexane instead of 5-percent acetone in hexane for F2. F2 solvent contains less than 5-percent acetone. Incorrect sorbent activation or deactivation.
No surrogates in F1 or F2	Forgot to add surrogates to sample. Incorrect sorbent activation or deactivation.

Surrogate recoveries from reagent OC spike and reagent blank samples are used to evaluate method performance under noninterfering (matrix-free) conditions. Surrogate recoveries in field-sediment samples that are significantly different from mean recoveries observed for the reagent OC spike and reagent blank samples might indicate sample-specific, matrix-related bias problems. These problems can range from matrix interferences in the quantitation of select compounds to sample preparation problems that bias the recovery of all method compounds (see following Laboratory Quality Assurance section).

Mean surrogate recoveries for 270 field-sediment samples and associated quality-control samples were comparable to the mean recoveries measured for the reagent OC spike and reagent blank samples only (table 13). Mean recoveries for PCB-204 were improved when the OC surrogate solution (5.2.4) was prepared in hexane instead of methanol (table 13). The other two surrogates seem unaffected by choice of solution solvent.

Table 13.--*Surrogate recoveries from reagent blank and reagent organochlorine spike samples in relation to 270 field-sediment and quality-control samples*

| | Reagent blank and OC spike samples | | | | | | |
| Surrogate | 26 samples from sets 93139C through 93235A[a] | | 33 samples from sets 93291A through 94.110[b] | | Field-sediment and quality-control samples | | |
	Mean recovery (percent)	Standard deviation (percent)	Mean recovery (percent)	Standard deviation (percent)	Mean recovery (percent)	Standard deviation (percent)	Detects[c]
3,5-DCB	56	15	56	14	58	16	267
PCB-204	44	13	76	17	71	16	269
α-HCH-d$_6$	65	11	60	14	64	16	270

[a]Surrogate solution prepared in methanol.
[b]Surrogate solution prepared in hexane.
[c]Number of quantifiable detections.

Recovery results for standard reference materials--Recovery results for the National Institute of Standards and Technology's SRM 1941 organics in marine-sediment samples processed with 17 sets of samples are listed in table 14. SRM 1941 has been certified for 11 polycyclic aromatic hydrocarbons (PAH), with noncertified concentrations provided for 24 additional PAH, 7 OC pesticides, and 15 PCB congeners (National Institute of Standards and Technology, 1989; Schantz and others, 1990). It also contains 1.7 percent sulfur. This SRM was used as a quality-assurance material because of its suitability for testing the optional SVOC portion of the method (fig. 1). The PAH are present in SRM 1941 at approximately one to four orders of magnitude higher concentrations than the noncertified OC pesticides. The high PAH concentrations, coupled with SRM cost and availability considerations, resulted in the use of only about 4 g of SRM per extraction, instead of the typical 25-g sample size. Therefore, the effective reporting limits for the 4-g SRM samples would be six times higher than the interim reporting limits for a 25-g sample size shown in table 8. Of the seven noncertified OC pesticides in SRM 1941, only p,p'-DDD and p,p'-DDE have concentrations greater than the revised reporting limits for a 4-g sample size (table 14). Nevertheless, attempts were made to quantitate the noncertified pesticides at less than the revised reporting limits. The mean recoveries for cis-chlordane, trans-nonachlor, p,p'-DDD, and p,p'-DDE ranged from 70 to 97 percent. Dieldrin and p,p'-DDT had unusually high recoveries, likely because of instrumental imprecision or interferences at these low "noise-level" concentrations. Heptachlor epoxide was not detected. Four other compounds--HCB, trans-chlordane, cis-nonachlor, and total PCBs--also were detected and quantified in the SRM (table 14).

Table 14.—*Recovery of noncertified and other detected compounds from the National Institute of Standards and Technology's (NIST) organics in marine sediment standard reference material 1941 processed with 17 sets*

[µg/kg, micrograms per kilogram; g, gram; ±, plus or minus; <, less than; nd, not detected; –, not given; na, not applicable]

Compounds[a]	Noncertified concentration and standard deviation[b] (µg/kg)	Revised reporting limit for 4-g sample[c] (µg/kg)	NIST standard reference material 1941				
			Mean determined concentration (µg/kg)	Standard deviation (µg/kg)	Mean recovery (percent)	Standard deviation (percent)	Number of detects
Noncertified compounds							
cis-Chlordane	2.06 ± 0.05	<6	1.7	0.9	81	42	17
p,p'-DDD	10.3 ± 0.1	<6	8.1	3.4	78	33	16
p,p'-DDE	9.71 ± 0.17	<6	6.8	1.4	70	15	17
p,p'-DDT	1.11 ± 0.05	<12	3.9	2.2	348	196	12
Dieldrin	0.63 ± 0.03	<6	1.5	0.4	236	59	9
Heptachlor epoxide	0.23 ± 0.02	<6	nd	–	–	–	0
trans-Nonachlor	0.97 ± 0.03	<6	0.9	0.7	97	71	14
Other compounds							
trans-Chlordane	–	<6	2.3	0.9	na	na	17
Hexachlorobenzene	–	<6	18	3.6	na	na	17
cis-Nonachlor	–	<6	2.7	1.4	na	na	13
PCBs (total)	–	<300	332	64	na	na	17
Surrogates							
3,5-DCB	na	–	–	–	61	12	17
PCB-204	na	–	–	–	61	14	17
alpha-HCH-d$_6$	na	–	–	–	59	9	17

[a]Only compounds having reported noncertified values or that were detected on both columns are shown.

[b]NIST's noncertified concentrations (National Institute of Standards and Technology, 1989; Schantz and others, 1990).

[c]Method reporting levels are raised by a factor of six greater than those shown in table 8 because only 4 g of reference material was extracted instead of the normal 25-g dry-weight sample size.

Recovery results for Environmental Resource Associates' spiked organics in soil reference material CLP720, processed with sets 93145B and 93145C, are listed in table 15. This spiked garden soil SRM has concentrations of OCs that are about 6 to 350 times greater than the natural concentrations in SRM 1941. The determined concentrations are within the advisory ranges from Environmental Resource Associates. These advisory ranges are provided as guidelines for acceptable recoveries given the limitations of the USEPA methodologies commonly used to determine these compounds.

Table 15.--*Amount of compound recovered in relation to the certified concentration and advisory range for Environmental Resource Associates' spiked organics in soil reference material CLP720 processed with sets 93145B and 93145C*

[μg/kg, micrograms per kilogram; --, not given; na, not applicable]

| Compound[b] | Soil reference material CLP720, lot number 318[a] | | | | | |
| | Certified amount[c] (μg/kg) | Advisory range[c] (μg/kg) | Amount recovered for set 93145B | | Amount recovered for set 93145C | |
			(μg/kg)	(percent)	(μg/kg)	(percent)
Aldrin	49.1	21–60	31	63	35	71
trans-Chlordane	45.8	14–59	34	74	31	68
cis-Chlordane	88.2	26–110	54	61	54	61
p,p'-DDD	222	69–310	(d)	--	(d)	--
p,p'-DDE	62.8	19–91	40	64	54	86
p,p'-DDT	29.2	7.3–47	22	75	13	45
Dieldrin	77.3	28–110	61	79	53	69
Endrin	39.1	12–58	26	66	30	77
beta-HCH	85.2	14–130	66	77	59	69
Heptachlor	95.2	32–110	53	56	62	65
Heptachlor epoxide	80.5	30–110	65	81	61	76
Surrogates						
3,5-DCB	na	na	--	45	--	68
PCB-204	na	na	--	93	--	72
α-HCH-d$_6$	na	na	--	86	--	66

[a]Environmental Resource Associates' PriorityPollutnT™/CLP Quality Control Standards-- Spiked Semivolatiles in Soil, catalog number 720, lot number 318, Arvada, Colorado.

[b]Only identified compounds with certified values are shown.

[c]Certified concentrations and advisory ranges from Environmental Resource Associates. The advisory ranges are provided as guidelines for acceptable recoveries given the limitations of the U.S. Environmental Protection Agency methodologies commonly used to determine these compounds.

[d]p,p'-DDD was not quantitated because of coelution with other method compounds in calibration standards on both columns.

Laboratory duplicate sample analysis results--One laboratory duplicate sample was processed with each set of samples, and was selected at random from one of the field samples within the set. The duplicate analysis provides an indication of method precision within that particular matrix. A summary of the detections in, and relative percent difference (*RPD*) between, laboratory duplicate samples extracted in 34 sets is listed in table 16. For most duplicates, there were no detections of any method compounds in either extract. When a compound was quantitated in only one of the duplicates, the reported concentration was at the interim reporting limit. Mean *RPDs* were calculated using samples where compounds were quantitated in both duplicates. The mean *RPDs* for most compounds were less than 26 percent, except for one duplicate sample containing DCPA. The USEPA's relative percent difference acceptance limits for six OC pesticides established for the Contract Laboratory Program (U.S. Environmental Protection Agency, 1991) also are listed in table 16. The mean *RPDs* for *p,p'*-DDT and dieldrin (only comparable *RPDs*) are well within the USEPA limits.

Table 16.--*Detections in, and relative percent difference between, laboratory duplicate samples extracted in 34 sets*

[USEPA, U.S. Environmental Protection Agency; --, not available]

Compound	Number of nondetects in sample and duplicate	Number of detects in sample in relation to nondetects in duplicate	Number of detects in sample and duplicate	Mean relative percent difference[a] (percent)	USEPA relative percent difference acceptance limit[b] (percent)
Aldrin	34	0	0	--	43
cis-Chlordane[c]	30	0	3	18	--
trans-Chlordane	30	[d] 1	3	25	--
Chloroneb[c]	32	0	0	--	--
DCPA	32	[d] 1	1	105	--
o,p'-DDD[c]	17	0	2	16	--
p,p'-DDD[c]	16	0	1	16	--
o,p'-DDE	33	0	1	24	--
p,p'-DDE	26	0	8	5	--
o,p'-DDT[c]	17	[d] 1	2	6	--
p,p'-DDT[c]	16	0	3	9	50
Dieldrin	31	0	3	14	38
Endosulfan I	34	0	0	--	--
Endrin	34	0	0	--	45
HCB	33	0	1	19	--
α-HCH	34	0	0	--	--

Table 16.--*Detections in, and relative percent difference between, laboratory duplicate samples extracted in 34 sets*--Continued

Compound	Number of nondetects in sample and duplicate	Number of detects in sample in relation to nondetects in duplicate	Number of detects in sample and duplicate	Mean relative percent difference[a] (percent)	USEPA relative percent difference acceptance limit[b] (percent)
β-HCH	33	[d]1	0	--	--
γ-HCH	34	0	0	--	50
Heptachlor	34	0	0	--	31
Heptachlor epoxide	34	0	0	--	--
Isodrin	34	0	0	--	--
o,p'-Methoxychlor[c]	23	0	0	--	--
p,p'-Methoxychlor[c]	23	0	0	--	--
Mirex	34	0	0	--	--
cis-Nonachlor	33	[d]1	0	--	--
trans-Nonachlor	31	[d]2	[d]1	24	--
Oxychlordane[c]	33	0	0	--	--
Pentachloroanisole	34	0	0	--	--
cis-Permethrin[c]	27	0	2	9	--
trans-Permethrin[c]	26	0	2	12	--
PCBs (total)	34	0	0	--	--
Toxaphene	34	0	0	--	--
Surrogates					
3,5-DCB	0	0	34	16	--
PCB-204	0	0	34	15	--
α-HCH-d$_6$	0	0	34	17	--

[a]The relative percent difference (*RPD*) is calculated as follows:

$$RPD = \left| \frac{C_1 - C_2}{(C_1 + C_2)/2} \right| \times 100$$

where C_1 and C_2 are the compound concentrations in the duplicate samples.

[b]USEPA relative percent difference acceptance limits are from the Contract Laboratory Program (U.S. Environmental Protection Agency, 1991).

[c]For these compounds, the listed numbers of detects and nondetects do not total 34 because of quantification difficulties related to coelution, matrix-interference, or gas chromatograph-degradation (DDTs and methoxychlors) problems.

[d]Concentrations at reporting limit.

LABORATORY QUALITY ASSURANCE

The GC/ECD performance criteria were described in section 11.2. Overall method quality assurance is assessed using the various quality-control samples processed with each set of field samples, along with the sample-specific surrogate recoveries. U.S. Environmental Protection Agency (1990c, chap. 1, p. 17) methods require that "Control limits be established to evaluate laboratory precision and bias based on the analysis of control samples. Typically, control limits for bias are based on the historical mean recovery plus or minus three standard deviation units (±3 sigma), and the control limits for precision range from zero (no difference between duplicate control samples) to the historical mean relative percent difference plus three standard deviation units." The NWQL has adopted this definition of control limits for bias for organic methods, and also established warning limits for bias at ±2 sigma of the mean recovery (Friedman and Erdmann, 1982, p. 91-99).

For example, the warning and control limits for bias applicable to field samples from sets 93291A through 94.110 could be established using the reagent OC spike sample recovery data in table 11 and the reagent OC spike and reagent blank surrogate recovery data in table 13. The NWQL provides regular updates of these limits for its customers.

Verification of standard solution concentrations is another critical quality-assurance requirement. During implementation of this method, solution changes, particularly of spike and surrogate standards that were more rapidly consumed, were found to result in statistically significant changes in determined recoveries (Appendix B). Verify compound concentrations in all in-house or commercially prepared calibration and spiking standards prior to their use. Third-party check standards (for example, standard reference solutions from the National Institute of Standards and Technology) can be used to assist in this verification process, provided the original sources of the pesticides used to prepare the TPCs are not the same sources used to prepare the solutions being verified.

CONCLUSIONS

Since May 1993, this analytical method has been used routinely for the determination of 30 individual organochlorine pesticides, total toxaphene, and total polychlorinated biphenyls in bottom sediment. Results from quality-assurance samples and of surrogate recoveries determined with nearly 30 sets of field-sediment samples have defined method performance to date (February 1995). Interim reporting limits range from 1- to 5-µg/kg dry-sediment weight for the OC pesticides, 50 µg/kg for total PCBs, and 200 µg/kg for total toxaphene. These reporting limits may change following additional method-detection-limit determinations.

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Method 3540B--Soxhlet extraction, rev. 2, p. 3540B 1-8;
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Method 3640A--Gel-permeation cleanup, rev. 1, p. 3640A 1-24;
Method 8080A--Organochlorine pesticides and polychlorinated biphenyls by gas chromatography, rev. 1, p. 8080A 1-28;
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RELEVANT NWQL STANDARD OPERATING PROCEDURES

(Please consult the most recent version of these standard operating procedures. Standard operating procedures can be provided on request to: Chief, Branch of Analytical Services, NWQL.)

Furlong, E.T., 1994, Preparation of sediments containing semivolatile organic compounds and organochlorine compounds: Standard operating procedure no. MS0004.1.

Merten, L.M., and Furlong, E.T., 1994, Gel permeation chromatography cleanup of NAWQA sediments using the Waters HPLC: Standard operating procedure no. MS0024.0.

Connor, B.F., and Pirkey, K.D., 1994, Analysis of organochlorine insecticides and PCBs in sediment--Schedule 2501: Standard operating procedure no. OS0021.0.

APPENDIX A

PRELIMINARY PERFORMANCE RESULTS
FOR THE ORIGINAL METHOD

Substantial procedural differences between the original method tested during method development and the foregoing final method implemented on May 19, 1993, are summarized in this appendix. The preliminary method-performance data collected with the original method also are summarized below. Additional method changes that were adopted on implementation of the method January 7, 1993, through March 19, 1993, are briefly summarized in Appendix B specifically for the USGS National Water-Quality Assessment program.

ORIGINAL METHOD PROCEDURAL DIFFERENCES

The procedural differences summarized below are listed in sections comparable to the final method procedure already described. The reason for the changes to the final method procedure are briefly noted under each section.

A.1   Sediment extract concentration

A.1.1   The extract was increased from a volume range of 0.3 to 0.4 mL up to a volume of 3 mL (7.3.3) prior to filtration.

Note: The use of a greater final extract volume prior to GPC in the final method was required by the Waters GPC autosampler system. The greater extract volume also reduced the amount of precipitate that regularly occurs with further volume reduction. This precipitate reduces injection reliability by the GPC system. Sample handling at smaller volumes also is more difficult.

A.2   Sediment extract filtration

A.2.1   A centrifugation step (7.4.1) was added prior to filtration.

Note: Centrifugation improves the filtration process.

A.2.2   The receiver tube rinse volume was increased from 300 µL dichloromethane up to 500 µL (7.4.6).

Note: The use of larger extract volumes (see A.1 note) allowed for slightly larger rinse volumes.

A.3   Gel permeation chromatography

A.3.1   A Hewlett-Packard model 1090 high-performance liquid chromatograph was replaced with the Waters GPC system (4.5.1).

Note: The Hewlett-Packard HPLC was used as a temporary GPC system prior to the acquisition of a system designed specifically for handling GPC cleanup. The Waters GPC provided improved recoveries.

A.3.2   The GPC injection-volume conditions were changed from 400 µL out of a 1-mL final extract volume to 1,100-µL injection volume (7.5.9) out of a 4-mL final extract volume (7.4.8) for the OC compounds.

See A.1 Note.

A.4   Adsorption chromatography cleanup and fractionation

A.4.1   The fraction 2 solvent was changed from 25 mL of a one-to-one mixture of acetone and hexane to 35 mL of a 5-percent acetone in hexane mixture (7.7.15).

Note: The percentage of acetone was lowered to 5 percent for the final method to provide a cleaner F2 extract and to help minimize degradation of DDT and other labile compounds in the GC injection port. However, this change resulted in incomplete recoveries of endosulfan II, endosulfan sulfate, endrin aldehyde, and endrin ketone in F2. Therefore, these four compounds are not included as final method compounds (see table 10). Additional (intermediate) changes in F2 solvent occurred between implementation of the method on January 7, 1993, and final method implementation on May 19, 1993, and these changes are outlined in Appendix B.

A.5   Fraction concentration

A.5.1   The final extract volume prior to GC/ECD was decreased from 1 to 0.5 mL (7.8.3).

Note: A 0.5-mL final extract volume was implemented to lower method reporting limits.

PERFORMANCE RESULTS FOR THE ORIGINAL METHOD

Usually method performance is tested by establishing the recoveries of the method compounds spiked at a minimum of two concentration levels in at least three different matrices. A minimum of seven replicate determinations needs to be performed at each test condition. For the original method, the matrices tested included a reagent (sodium sulfate) and two natural sediments, Mississippi River and Evergreen Lake, Colorado, bottom sediment. Unfortunately, limited development time prohibited the completion of a full method-performance-evaluation study. In addition, operational problems encountered with use of the Hewlett-Packard HPLC system for GPC or during GC/ECD analysis rendered substantial numbers of the test samples or portions of the recovery data unusable. The preliminary method-performance data obtained using the original method are listed in tables 17 through 19. These data include mean recovery and

precision data for the individual OC pesticides spiked at 20 μg/kg into sodium sulfate, assuming a 25-g sample size (table 17), at 20 μg/kg into Mississippi River sediment (table 18), and at 1.6 μg/kg into Evergreen Lake sediment (table 19). For the environmental sediment samples, the recovered amounts were corrected for the amount of ambient OC pesticides determined in the unspiked sediment. The mean recovery of toxaphene from triplicate sodium sulfate reagent-spike samples at 320 μg/kg also is listed in table 17.

Table 17.--*Mean recovery of method and other tested pesticides from four replicate sodium sulfate reagent samples spiked at 20 micrograms per kilogram*[a]

[ni, not in spike solution; --, not determined]

Compound	Mean recovery[b] (percent)	Standard deviation (percent)	Relative standard deviation (percent)
Aldrin	66	4	6
cis-Chlordane	77	7	9
trans-Chlordane	60	5	9
Chloroneb	68	5	8
Chlorothalonil[c]	22	18	84
DCPA	87	9	11
o,p'-DDD	84	9	10
p,p'-DDD	78	10	13
o,p'-DDE	66	4	6
p,p'-DDE	57	3	6
o,p'-DDT	65	14	22
p,p'-DDT	61	15	24
Dieldrin	72	8	12
Endosulfan I	54	11	21
Endosulfan II[c]	19	6	34
Endosulfan sulfate[c]	94	14	15
Endrin	54	15	28
Endrin aldehyde[c]	24	5	21
Endrin ketone[c]	73	13	18
HCB	72	4	5
alpha-HCH	67	10	15
beta-HCH	84	10	12
delta-HCH[c]	16	12	73
gamma-HCH	69	9	14
Heptachlor	73	5	7
Heptachlor epoxide	78	7	10

Table 17.--*Mean recovery of method and other tested pesticides from four replicate sodium sulfate reagent samples spiked at 20 micrograms per kilogram[a]*--Continued

Compound	Mean recovery[b] (percent)	Standard deviation (percent)	Relative standard deviation (percent)
Hexachlorobutadiene[c]	72	2	3
Hexachlorocyclopentadiene[c]	59	7	12
Isodrin	70	4	6
o,p'-Methoxychlor	79	16	20
p,p'-Methoxychlor	62	20	32
Mirex	75	6	8
cis-Nonachlor	78	8	10
trans-Nonachlor	81	7	8
Oxychlordane	81	7	9
Pentachloroanisole	72	8	11
cis-Permethrin	86	15	18
trans-Permethrin	87	14	16
Perthane[c]	86	9	10
Toxaphene[d]	67	24	35
Surrogates			
3,5-DCB	24	2	9
PCB-204	ni	--	--
alpha-HCH-d_6	60	7	12

[a]Spike concentration assuming a 25-gram sample size.

[b]Number of detections for all spiked compounds, except toxaphene, was four.

[c]Compound tested during initial method-performance evaluations but not included as a final method compound because of performance problems.

[d]Mean recovery for toxaphene fortified at 320 micrograms per kilogram (assuming a 25-gram sample size) from triplicate sodium sulfate reagent-spike samples.

Appendix A

Table 18.--*Mean recovery of method and other tested pesticides from six replicate Mississippi River sediment samples spiked at 20 micrograms per kilogram*

[ni, not in spike solution; --, not determined]

Compound	Mean recovery[a] (percent)	Standard deviation (percent)	Relative standard deviation (percent)
Aldrin	84	4	5
cis-Chlordane	78	8	11
trans-Chlordane	80	10	13
Chloroneb	ni	--	--
Chlorothalonil[b]	44	11	26
DCPA	74	10	14
o,p'-DDD	103	11	10
p,p'-DDD	120	14	12
o,p'-DDE	ni	--	--
p,p'-DDE	97	9	9
o,p'-DDT	59	10	18
p,p'-DDT	69	8	12
Dieldrin	76	10	13
Endosulfan I	74	9	13
Endosulfan II[b]	31	3	9
Endosulfan sulfate[b]	79	8	10
Endrin	78	6	8
Endrin aldehyde[b]	28	7	26
Endrin ketone[b]	100	19	19
HCB	99	5	5
alpha-HCH	78	12	15
beta-HCH	93	19	20
delta-HCH[b]	74	12	17
gamma-HCH	85	9	10
Heptachlor	39	6	16
Heptachlor epoxide	79	10	12
Hexachlorobutadiene[b]	ni	--	--
Hexachlorocyclopentadiene[b]	ni	--	--
Isodrin	86	5	6
o,p'-Methoxychlor	76	11	14
p,p'-Methoxychlor	82	9	11
Mirex	79	9	11
cis-Nonachlor	ni	--	--
trans-Nonachlor	82	9	11
Oxychlordane	83	10	12

Table 18.--*Mean recovery of method and other tested pesticides from six replicate Mississippi River sediment samples spiked at 20 micrograms per kilogram*--Continued

Compound	Mean recovery[a] (percent)	Standard deviation (percent)	Relative standard deviation (percent)
Pentachloroanisole	ni	--	--
cis-Permethrin	102	11	11
trans-Permethrin	100	14	14
Perthane[b]	66	11	16
Surrogates			
3,5-DCB	ni	--	--
PCB-204	ni	--	--
alpha-HCH-d$_6$	81	13	16

[a]Number of detections for all spiked compounds was six.

[b]Compound tested during initial method-performance evaluations but not included as a final method compound because of performance problems.

Table 19.--*Mean recovery of method and other tested pesticides from four replicate Evergreen Lake, Colorado, sediment samples spiked at 1.6 micrograms per kilogram*

[nd, not detected; --, not determined; ni, not in spike solution]

Compound	Mean recovery[a] (percent)	Standard deviation (percent)	Relative standard deviation (percent)
Aldrin	42	7	16
cis-Chlordane	58	8	13
trans-Chlordane	52	10	19
Chloroneb	59	8	13
Chlorothalonil[b]	26	7	25
DCPA	92	13	14
o,p'-DDD	66	10	16
p,p'-DDD	64	15	24
o,p'-DDE	48	7	14
p,p'-DDE	35	7	19
o,p'-DDT	48	16	34
p,p'-DDT	61	17	27
Dieldrin	43	7	16
Endosulfan I	48	7	16
Endosulfan II[b]	19	5	25

Table 19.--*Mean recovery of method and other tested pesticides from four replicate Evergreen Lake, Colorado, sediment samples spiked at 1.6 micrograms per kilogram*--Continued

Compound	Mean recovery[a] (percent)	Standard deviation (percent)	Relative standard deviation (percent)
Endosulfan sulfate[b]	57	12	22
Endrin	46	8	17
Endrin aldehyde[b]	45	8	18
Endrin ketone[b]	53	9	16
HCB	68	19	28
alpha-HCH	44	9	21
beta-HCH	52	10	18
delta-HCH[b]	36	6	16
gamma-HCH	42	7	16
Heptachlor	52	4	8
Heptachlor epoxide	54	8	14
Hexachlorobutadiene[b]	32	22	69
Hexachlorocyclopentadiene[b]	nd	--	--
Isodrin	43	8	18
o,p'-Methoxychlor	77	12	16
p,p'-Methoxychlor	68	10	15
Mirex	64	10	16
cis-Nonachlor	52	8	16
trans-Nonachlor	66	10	16
Oxychlordane	66	9	14
Pentachloroanisole	56	9	16
cis-Permethrin	54	6	12
trans-Permethrin	55	22	39
Perthane[b]	91	12	13
Surrogates			
3,5-DCB	ni	--	--
PCB-204	ni	--	--
alpha-HCH-d_6	55	10	18

[a]Number of detections for all spiked compounds, except hexachlorocyclopentadiene, was four.

[b]Compound tested during initial method-performance evaluations but not included as a final method compound because of performance problems.

Partial PCB recovery results--Mean recovery and precision data for total PCBs from one sodium sulfate reagent-spike sample processed using the original method and two reagent-spike samples processed prior to implementation of the final method March 19, 1993, are listed in table 20. The spikes were fortified at 200 ng each of Aroclor 1016, 1254, and 1260, providing a total PCB amount of 600 ng, or a concentration of 24 µg/kg assuming a 25-g sample size.

Table 20.--*Mean recovery of total PCBs from triplicate sodium sulfate reagent samples spiked with PCBs at 24 micrograms per kilogram assuming a 25-gram sample size*[a]

Compound	Mean recovery (percent)	Standard deviation (percent)	Relative standard deviation (percent)
PCBs (total)	67	7	11
Surrogates			
3,5-DCB	69	40	57
PCB-204	57	33	57
alpha-HCH-d$_6$	41	18	43

[a]Set PCB spike samples processed with sets 92POTOMAC, 930007A, and 93123B.

APPENDIX B

SUMMARY OF METHOD MODIFICATIONS FOLLOWING IMPLEMENTATION AND THE RESULTANT EFFECTS ON DATA QUALITY

This appendix has been included to officially document several important methodological changes and other method-related issues relevant to the first 20 NAWQA Study Units that had sediment samples analyzed under sets 93007A through 93235A by the NWQL.

The significant procedural changes to the method that were made upon or following method implementation January 7, 1993 (sample set 930007A), up to March 19, 1993 (sample set 93139C), when the final method was implemented, and the resultant effects on sample data quality are summarized in table 21. The effects on data quality of changes in individual OC spike and surrogate solutions used for sets 93007A through 93235A are listed in table 22. The impacts of two GC analysis issues on sample data quality are summarized in table 23.

Complete details regarding all of the above changes and the resultant impacts on data quality were provided to the first 20 NAWQA Study Units in an unpublished USGS memorandum entitled "Guidance on use of quality-control data for Schedule 2501--Organochlorine compounds in bottom material" issued January 20, 1994, by the NAWQA/NWQL Quality Assurance Committee for Organics in Bed Sediment. Copies of this memorandum may be obtained by writing to:

> U.S. Geological Survey
> Chief, Methods Research and Development Program
> National Water Quality Laboratory
> Box 25046, Mail Stop 411
> Federal Center
> Denver, CO 80225

Table 21.--Summary of the effects of methodological improvements on sample data quality

[NAWQA, National Water-Quality Assessment program; F2, fraction 2; mL, milliliters]

Methodological improvements	Sets applied	NAWQA Study Units affected	Compounds affected	Probable impact on field sample data quality	Effect on recoveries in reagent organochlorine spike samples
I. Gel permeation chromatography system used					
a) Hewlett-Packard	93007A through 93022A	Four only[a]	All	Lower recoveries for most compounds in all sample types.	Low recoveries for 93007A through 93022A.
b) Waters	93032A through 93235A	Various	All	Improved recoveries.	Improved recoveries for 93032A through 93235A.
II. Alumina/silica adsorption chromatography F2 solvent changes					
a) Solvent mix A[b] (F2: 25 mL of 10-percent acetone in hexane)	93007A through 93081A	Various	Only endrin ketone and endosulfan sulfate.	Low recoveries. Treat as "qualitative estimates" in all samples. Nondetects are not necessarily indicative of absence.	Low recoveries for 93007A through 93081A.
b) Solvent mix B (F2: 25 mL of 15-percent acetone in hexane)	93109A through 93133B	Various	Only endrin ketone and endosulfan sulfate.	Improved recoveries. Data OK.	Improved recoveries for 93109A through 93133B.
c) Solvent mix C (F2: 35 mL of 5-percent acetone in hexane)	93137A through 93235A	Various	Only endrin ketone, endosulfan II, and endosulfan sulfate.	Compounds not recovered and <u>deleted</u> from method.	Incomplete recoveries and compounds deleted for 93137A through 93235A.

[a]Only Central Columbia Plateau, Georgia/Florida, Red River of the North, and Willamette Study Units had samples in sets 93007A through 93022A.

[b]The amount and composition of solvent mix A is different from the F2 solvent mix used during initial method development (see A.4.1).

Appendix B

Table 22.--*Summary of the effects of spike or surrogate solution changes on sample data quality*

[NAWQA, National Water-Quality Assessment program]

Solution changes	Sets applied	NAWQA Study Units affected	Compounds affected	Probable impact on field sample data quality	Effect on recoveries in reagent organochlorine spike samples
I. Individual organochlorine pesticide spike solution changes	Solution changed beginning at set 93109A.	All	Only *cis*-chlordane, DCPA, dieldrin, heptachlor, isodrin, and *cis*-nonachlor.	**None** / Spike solution change affected reagent organochlorine spike sample recoveries <u>only</u>.	Recovery changes between sets 93007A through 93081A and 93109A through 93235A.
II. Organochlorine surrogate solution changes	Solution changed 3 times beginning at sets 93109A, 93139A, and 93165A.	Various	3,5-DCB	**No direct effect on method compounds.** / 3,5-DCB recoveries may be somewhat higher in sets 93165A through 93235A.	3,5-DCB recovery higher in sets 93165A through 93265A.
			PCB-204	Lower recoveries for PCB-204 in sets 93139A through 93235A do not reflect preparation problems unless less than 18 percent (the lower 3-sigma control limit for these sets).	PCB-204 recovery lower in sets 93139A through 93235A.

Table 23.--Summary of the effects of gas chromatography analysis issues on sample data quality

[NAWQA, National Water-Quality Assessment program; RL, reporting level; >, greater than; <, less than]

Instrumental analysis issues	Sets applied	NAWQA Study Units affected	Compounds affected	Probable impact on field sample data quality	Effect on recoveries in reagent organochlorine spike samples
I. Coelution of method compounds on both gas chromatographic capillary columns (an instrument/column-dependent problem).	All	All	Only p,p'-DDD, o,p'-DDE, endosulfan I, cis-nonachlor, and oxychlordane.	How data reported under coelution situations: Peak detected? / Value reported[a] Yes at >RL / Raised RL or D-U Yes at < RL / < RL No / < RL	Coelutions in reagent spike samples noted on control charts.
II. Degradation of thermally labile compounds during gas chromatographic analysis.	93007A through 93133B. Also rarely in later sets.	Various	o,p'-DDT, p,p'-DDT, endrin, endrin ketone, o,p'-methoxychlor, p,p'-methoxychlor. {Also o,p'-DDD and p,p'-DDD because these are primary degradation products of the parent DDT.}	Degradation monitored during analysis using the performance evaluation mixture standard. Reporting conditions: Observed degradation / Value reported[a] <30 percent / Actual value >30 percent (DDTs only) / D-M and ΣDDX=DDT+DDD+DDE[b] >30 percent (Other compounds) / Deleted (D-U or D-M)	None apparent.

[a]Reporting codes for deletions: D-U, deleted because of interference; D-M, deleted with explanation provided by memo.

[b]Sum of (Σ) p,p'-DDX = p,p'-DDT + p,p'-DDD + p,p'-DDE, and similarly for $\Sigma o,p'$-DDX.