



Designation: D 4861 – 00

Standard Practice for Sampling and Selection of Analytical Techniques for Pesticides and Polychlorinated Biphenyls in Air¹

This standard is issued under the fixed designation D 4861; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the sampling of atmospheres for a variety of common pesticides and polychlorinated biphenyls (PCBs) and provides guidance on the selection of appropriate analytical measurement methods.

1.2 A complete listing of pesticides and other semivolatile organic chemicals for which this practice has been tested is shown in Table 1.

1.3 This practice is based on the adsorption of chemicals from air on polyurethane foam (PUF) or a combination of PUF and granular sorbent.

1.4 This practice is applicable to multicomponent atmospheres, 0.001 to 50-μg/m³ concentrations, and 4 to 24-h sampling periods. The limit of detection will depend on the nature of the analyte and the length of the sampling period.

1.5 The analytical method(s) recommended will depend on the specific chemical(s) sought, the concentration level, and the degree of specificity required.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazards statements, see 10.24 and A1.1.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres³

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)³

D 3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method³

¹ This practice is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol 11.03.

D 4185 Practice for Measurement of Metals in Workplace Atmosphere by Atomic Absorption Spectrophotometry³

E 355 Practice for Gas Chromatography Terms and Relationships⁴

2.2 EPA Methods:⁵

EPA 600/4-89-017 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

EPA 600/R-96/010b Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

EPA 821/C-97-001 Methods and Guidance for Analysis of Water

EPA SW-846 Test Methods for Evaluating Solid Waste Physical Chemical Methods

2.3 Government Standard:⁵

40 CFR 136 EPA Organic Chemical Analysis of Municipal and Industrial Wastewater

3. Terminology

3.1 *Definitions*—Refer to Terminology D 1356 and Practice E 355 for definitions of terms used in this practice.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *dynamic retention efficiency*—ability of the sampling medium to retain the solution spike when air or nitrogen is drawn through the sampling cartridge under normal operating conditions and for the duration of the test period. The dynamic RE is normally equal to or less than the SE.

3.2.2 *relative retention time, (RRT)*—ratio of RTs for two chemicals for the same chromatographic column and carrier gas flow rate, where the denominator represents a reference chemical.

3.2.3 *retention efficiency, (RE)*—ability of the sampling medium to retain a compound added (spiked) to it in liquid solution.

3.2.4 *retention time, (RT)*—time to elute a specific chemical from a chromatographic column, for a specific carrier gas flow rate, measured from the time the chemical is injected into the gas stream until it appears at the detector.

3.2.5 *sampling efficiency, (SE)*—ability of the sampling medium to trap vapors of interest. The percentage of the

⁴ Annual Book of ASTM Standards, Vol 14.02.

⁵ Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.



TABLE 1 Compounds for Which Procedure Has Been Tested

Compound	Recommended Analysis ^A	Compound	Recommended Analysis
Alachlor	GC/ECD or MS	Heptachlor	GC/ECD or MS
Aldrin	GC/ECD or MS	Heptachlor epoxide	GC/ECD or MS
Allethrin	HPLC/UV or GC/MS	Hexachlorbenzene	GC/ECD or MS
Aroclor 1242	GC/ECD or MS	Hexachlorocyclopentadiene ^{B,C}	GC/ECD or MS
Aroclor 1254	GC/ECD or MS	Lindane (γ -HCH)	GC/ECD
Aroclor 1260	GC/ECD or MS	Linuron	HPLC/UV
Atrazine	GC/NPD or MS	Malathion	GC/NPD or FPD
Bendiocarb	HPLC/UV or GC/MS	Methyl parathion	GC/NPD or FPD
HCH (α - and β -Hexachlorocyclohexanes)	GC/ECD or MS	Methoxychlor	GC/ECD or MS
Captan	GC/ECD or MS	Metolachlor	GC/ECD or MS
Carbaryl	HPLC/UV or GC/MS	Mexacarbate	
Carbofuran	HPLC/UV or GC/MS	Mirex	GC/ECD or MS
Chlordane, technical	GC/ECD or MS	Monuron	HPLC/UV
Chlorothalonil	GC/ECD or MS	<i>trans</i> -Nonachlor	GC/ECD or MS
Chlorotoluron	HPLC/UV or GC/MS	Oxychlordane	GC/ECD or MS
Chlorpyrifos	GC/ECD or MS	Parathion	GC/NPD, FPD, or MS
Cyfluthrin	GC/ECD or MS	Pentachlorobenzene	GC/ECD or MS
2,4-D, acid, esters and salts	GC/ECD or MS ^D	Pentachlorophenol	GC/ECD or MS
Dacthal	GC/ECD or MS	Permethrin (<i>cis</i> and <i>trans</i>)	GC/MS
<i>p,p'</i> -DDT	GC/ECD or MS	<i>o</i> -Phenylphenol	HPLC/UV, GC/ECD, or MS
<i>p,p'</i> -DDE	GC/ECD or MS	Phorate	GC/NPD, FPD, or MS
Diazinon	GC/NPD, FPD, or MS	Propazine	GC/NPD or MS
Dicloran	GC/ECD or MS	Propoxur (Baygon)	GC/NPD or MS
Dieldrin	GC/ECD or MS	Pyrethrin	GC/MS
Dichlorvos (DDVP)	GC/ECD or MS	Resmethrin	GC/MS
Dicofol	GC/ECD or MS	Ronnel	GC/ECD or MS
Dicrotophos	HPLC/UV or GC/MS	Simazine	HPLC/UV or GC/MS
Diuron	HPLC/UV or GC/MS	Terbutiuron	HPLC/UV or GC/MS
Endrin	GC/ECD or MS	1,2,3,4-Tetrachlorobenzene ^B	GC/ECD or MS
Fenvalerate	HPLC/UV or GC/MS	1,2,3-Trichlorobenzene ^B	GC/ECD or MS
Fluometuron	HPLC/UV or GC/MS	2,4,5-Trichlorophenol	GC/ECD or MS
Folpet	GC/ECD or MS	Trifluralin	GC/ECD or MS
Fonophos	GC/NPD, FPD, or MS	Vinclozolin	GC/ECD, NPD, or MS

^A GC = gas chromatography; ECD = electron capture detector; FPD = flame photometric detector; HPLC = high-performance liquid chromatography; NPD = nitrogen-phosphorus detector; UV = ultraviolet absorption detector. (GC/MS (gas chromatography/mass spectrometry) is always recommended, if available.)

^B Using PUF/Tenax-GC "sandwich" trap.

^C Compound is very unstable in solution.

^D Derivatization necessary for free acid and salts.

analyte of interest collected and retained by the sampling medium when it is introduced as a vapor in air or nitrogen into the air sampler and the sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended use is indicated by % SE.

3.2.6 *static retention efficiency*—ability of the sampling medium to retain the solution spike when the sampling cartridge is stored under clean, quiescent conditions for the duration of the test period.

4. Summary of Practice

4.1 A low-volume (1 to 5 L/min) sampler is used to collect vapors on a sorbent cartridge containing PUF or PUF in combination with another solid sorbent. Airborne particles may also be collected, but the sampling efficiency is not known. The method is adopted from Ref (1)⁶ and is the basis of EPA 600/R-96/010b, Method TO-10A.

4.2 Pesticides and other chemicals are extracted from the sorbent cartridge with 5 % diethyl ether in hexane and may be determined by gas-liquid chromatography (GC) coupled with an electron capture detector (ECD), nitrogen-phosphorus detector (NPD), flame photometric detector (FPD), Hall electro-

lytic conductivity detector (HECD), or a mass spectrometer (MS). For some pesticides, high-performance liquid chromatography (HPLC) coupled with an ultraviolet (UV) detector or electrochemical detector may be preferable.

4.3 Interferences resulting from analytes having similar RTs during GC are resolved by improving the resolution or separation, such as by changing the chromatographic column or operating parameters, or by fractionating the sample by column chromatography.

5. Significance and Use

5.1 This practice is recommended for use primarily for non-occupational exposure monitoring in domiciles, public access buildings, and offices.

5.2 The methods described in this practice have been successfully applied to measurement of pesticides and PCBs in outdoor air and for personal respiratory exposure monitoring.

5.3 A broad spectrum of pesticides are commonly used in and around the house and for insect control in public and commercial buildings. Other semivolatile organic chemicals, such as PCBs, are also often present in indoor air, particularly in large office buildings. This practice promotes needed precision and bias in the determination of many of these airborne chemicals.

⁶ The boldface numbers in parentheses refer to the list of references at the end of this standard.

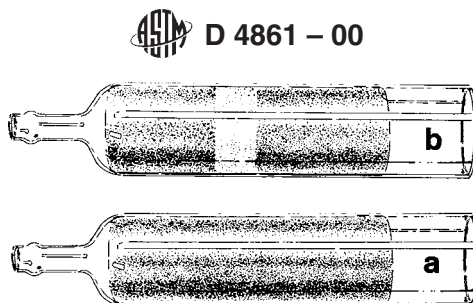


FIG. 1 PUF Sampling Cartridge (a) and PUF-Tenax GC Sampling Cartridge (b)

6. Interferences

6.1 Any gas or liquid chromatographic separation of complex mixtures of organic chemicals is subject to serious interference problems due to coelution of two or more compounds. The use of capillary or microbore columns with superior resolution or two columns of different polarity will frequently eliminate these problems.

6.1.1 Selectivity may be further enhanced by use of a MS in a selected ion monitoring (SIM) mode as the GC detector. In this mode, coeluting compounds can often be determined.

6.2 The ECD responds to a wide variety of organic compounds. It is likely that such compounds will be encountered as interferences during GC-ECD analysis. The NPD, FPD, and HECD detectors are element specific, but are still subject to interferences. UV detectors for HPLC are nearly universal and the electrochemical detector may also respond to a variety of chemicals. Mass spectrometric analyses will generally provide for positive identification of specific compounds.

6.3 PCBs and certain organochlorine pesticides (for example, chlordane) are complex mixtures of individual compounds, which can cause difficulty in accurately quantifying a particular formulation in a multiple component mixture. PCBs may also interfere with the determination of pesticides.

6.4 Contamination of glassware and sampling apparatus with traces of pesticides or PCBs can be a major source of error, particularly at lower analyte concentrations. Careful attention to cleaning and handling procedures is required in all steps of the sampling and analysis to minimize this source of error.

6.5 General approaches that can be followed to minimize interferences are as follows:

6.5.1 Polar compounds, including certain pesticides (for example, organophosphorus and carbamate classes) can be removed by column chromatography on alumina. This sample cleanup will permit the analysis of most organochlorine pesticides and PCBs (2).

6.5.2 PCBs may be separated from organochlorine pesticides by column chromatography on silicic acid. See Refs (3) and (4).

6.5.3 Many pesticides can be fractionated into groups by column chromatography on Florisil⁷ (4).

7. Apparatus

7.1 Air Sampler:

7.1.1 *Sampling Pump*, with a flow rate of 1 to 5 L/min. The pump should provide a constant air flow ($\leq \pm 5\%$) and be quiet and unobtrusive.

7.1.2 *Sampling Cartridge*, constructed from a 20-mm (inside diameter) $\times$ 10-cm borosilicate glass tube drawn down to a 7-mm (outside diameter) open connection for attachment to the pump by way of flexible tubing (see Fig. 1).

7.1.3 Sorbent, PUF, cut into a cylinder 22 mm in diameter and 7.6-cm long, and fitted under slight compression inside the cartridge. The PUF should be of the polyether type, density 0.022 g/cm³. This is the type of foam used for furniture upholstery, pillows, and mattresses. The PUF cylinders (plugs) should be cut slightly larger in diameter than the internal diameter of the cartridge. They may be cut by one of the following means:

7.1.3.1 With a high-speed cutting tool, such as a motorized cork borer. Distilled Type II water should be used to lubricate the cutting tool.

7.1.3.2 With a hot-wire cutter. Care is required to prevent thermal degradation of the foam.

7.1.3.3 With scissors, while compressed between two 22-mm circular templates.

7.1.4 Alternatively, pre-extracted PUF plugs and glass cartridges may be obtained commercially from one of several vendors.

7.1.5 *Particle Filter*, if desired, may be utilized. The collection efficiency of PUF for small-diameter (0.1 to 1 μ m) airborne particles is only about 20 % (5). However, most pesticides and PCBs exist in air under steady-state conditions, primarily as vapors (6). Most particulate-associated pesticides or PCBs, if any, will also tend to be vaporized from filters after collection (7). Collocated sampling with and without a quartz-fiber pre-filter has yielded indistinguishable results for a broad spectrum of pesticides and PCBs found in indoor air (8).

7.1.5.1 An open-face filter may be attached to the sampling cartridge by means of a union for 1-in. (25.4-mm) tubing. A 32-mm diameter micro-quartz-fibre, binderless, acid-washed filter is placed in the open end of the union and supported by means of a screen or perforated metal plate [for example, a 304 stainless steel disk, 0.0312-in. (0.8-mm) thick with $\frac{1}{16}$ -in. (1.6-mm) diameter round perforations at 132 holes/in². (20 holes/cm²), 41 % open area]. A 32-mm fluoroelastomeric or polytetrafluoroethylene (PTFE) O-ring is placed between the filter and outer nut to effect a seal (see Fig. 2).

7.1.6 *Size-Selective Impactor Inlet* with particle-size cut-points of either 2.5 or 10 μ m mean diameter at a sampling rate of 4 L/min may be used to exclude non-respirable airborne particulate matter (9, 10). An example of a sample with

⁷ Florisil is a trademark of the Floridin Corp., 5380 Capital Circle, N.W., Tallahassee, FL 32303. It is a natural magnesium silicate and is available from several commercial sources.

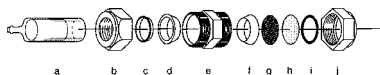


FIG. 2 Open-Face Filter Assembly: (a) Sampling Cartridge, (b) Inner Nut, (c) Back Ferrule, (d) Front Ferrule, (e) Union, (f) Front Ferrule, (g) Filter Support, (h) Filter, (i) Fluoroelastomeric or PTFE O-ring, (j) Outer Nut

size-selective inlet, particle filter support, sampling cartridge holder is shown in Fig. 3. This sampling cartridge is available commercially.

7.2 Equipment and Reagents for Sample Extraction and Concentration:

7.2.1 Round Bottom Flasks, 500 mL, § (standard paper glass joint) 24/40 joints,

7.2.2 Capacity Soxhlet Extractors, 300 mL, with reflux condensers,

7.2.3 Kuderna-Danish Concentrators, 500 mL, with Snyder columns,

7.2.4 Graduated Concentrator Tubes, 10 mL, with § 19/22 stoppers,

7.2.5 Graduated Concentrator Tubes, 1 mL, with § 14/20 stoppers,

7.2.6 TFE-fluorocarbon Tape, ½ in.,

7.2.7 Filter Tubes, size 40 mm (inside diameter) × 80 mm,

7.2.8 Vials, serum, 1 mL and 5 mL, fitted with caps lined with TFE-fluorocarbon,

7.2.9 Pasteur Pipets, 30 cm,

7.2.10 Glass Wool, fired at 500°C,

7.2.11 Boiling Granules, fired at 500°C,

7.2.12 Forceps, stainless steel, 23 cm,

7.2.13 Gloves, latex or polyvinyl acetate,

7.2.14 Steam Bath,

7.2.15 Heating Mantles, 500-mL size,

7.2.16 Analytical Evaporator, nitrogen blow-down apparatus with adjustable flow control and water bath with ± 5°C temperature control.

7.2.17 Acetone, pesticide quality⁸

7.2.18 *n*-Hexane, pesticide quality,⁸

7.2.19 Diethyl Ether, preserved with 2 % ethanol,

7.2.20 Sodium Sulfate, anhydrous, analytical grade, and

7.2.21 Solvents for HPLC, if required.

7.3 Purity of Reagents—Unless otherwise stated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁹ Other grades may be used, provided it is ascertained that use of the reagent does not lessen the accuracy of the test method.

7.4 Purity of Water—References to distilled water shall be understood to mean distilled water, which is Type II reagent water conforming to Specification D 1193.

7.5 Equipment for Analysis:

7.5.1 Gas Chromatograph (GC) with appropriate detector(s) and either an isothermally controlled or temperature programmed heating oven. Improved detection limits may be obtained with a GC equipped with a cool on-column or splitless injector.

7.5.2 Gas Chromatographic Columns, such as a 0.25 or 0.32-mm (inside diameter) × 30-m poly(5 %-diphenyl-95 %-dimethylsiloxane)¹⁰, (50 %-phenyl)-methylpolysiloxane¹¹ fused-silica, and others are commercially available.

7.5.3 HPLC Column, such as a 4.6-mm × 15-cm reversed-phase octadecyldimethylsilane (C-18) or porous silica gel. Other columns may also provide acceptable results.

7.5.4 Microsyringes, 5-μL volume or other appropriate sizes.

8. Sampling Procedure

8.1 For initial cleanup place the PUF plug in a Soxhlet extractor and extract with acetone for 14 to 24 h at 4 to 6 cycles/h. (If commercially pre-extracted PUF plugs are used, extraction with acetone is not required.) Follow with a 16-h Soxhlet extraction with 5 % diethyl ether in *n*-hexane. When cartridges are reused, 5 % ether in *n*-hexane can be used as the cleanup solvent.

8.2 Place the extracted PUF plugs in a vacuum oven connected to a water aspirator and dry at room temperature for 2 to 4 h (until no solvent odor is detected). Alternatively, they may be dried at room temperature in an air-tight container with circulating nitrogen (zero grade).

8.2.1 Place the PUF plug into a labeled glass sampling cartridge using gloves (see 7.2.13) and forceps. Wrap the cartridge with hexane-rinsed aluminum foil and place in glass jars fitted with TFE-fluorocarbon-lined caps. The foil wrapping may also be marked for identification using a blunt probe.

8.3 Granular sorbents may be combined with PUF to extend the range of use to compounds with saturation vapor pressures greater than 10⁻⁴ kPa (1). A useful combination trap can be assembled by “sandwiching” 0.6 g of a sorbent, such as 2,6-diphenyl-*p*-phenylene oxide (Tenax)¹² or styrene-divinylbenzene (XAD-2) polymer beads, between two 22-mm (diameter) × 3.8-cm pre-cleaned PUF plugs, as shown in Fig. 1, Cartridge b. The granular sorbent should be pre-extracted in accordance with 8.1. This trap may be extracted, vacuum dried, and removed without unloading it.

8.4 Analyze at least one assembled cartridge from each batch as a laboratory blank before the batch is considered

⁸ Glass distilled and certified for pesticides analysis by GC/ECD.

⁹ Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

¹⁰ This column is available from several commercial sources under such trade names as DB-5, SPB-5, Rtx-5, HP-5, OV-5, BP-5, and others.

¹¹ This column is available from several commercial sources under such trade names as DB-17, DB-608, SPB-17, SPB-608, HP-17, HP-608, OV-17, Rtx-50, and others.

¹² “Tenax” is a registered trademark of the Enka, N.V., and is commercially available from several suppliers.

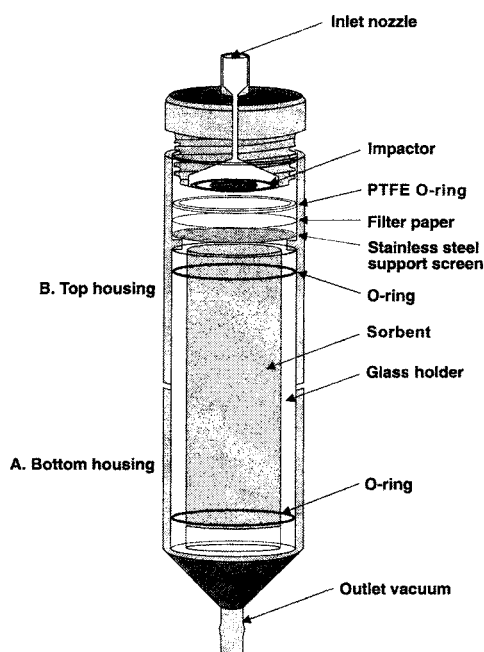


FIG. 3 Air Sampling Assembly with Size-selective Inlet, Particle Filter, and Glass Sorbent Cartridge

acceptable for use. A blank level of <10 ng/plug for single compounds is considered to be acceptable. For multiple component mixtures (for example, PCBs) the blank level should be <100 ng/plug.

8.5 After the sampling system has been assembled and calibrated in accordance with Section 9, it can be used to collect air samples as follows:

8.5.1 Sampling cartridges should be used within 30 days of loading.

8.5.2 Sampling cartridges should be handled only with clean latex or polyvinyl acetate plastic gloves.

8.5.3 Carefully remove aluminum foil wrappings from cartridges and return foil to jars for later use.

8.5.4 Attach cartridge to pump with flexible tubing and orient intake downward or in a horizontal position.

8.5.5 Locate sampler in an unobstructed area at least 30 cm from any obstacle to air flow.

8.5.6 Position cartridge intake 1 to 2 m above the floor or ground.

8.5.7 For outdoor applications, the pump and sampling cartridges should be sheltered from adverse weather conditions.

8.5.8 For personal exposure monitoring, the cartridge should be attached (inlet downward) to the clothing near the breathing zone by means of a suitable fastener and the pump may be attached to a waist belt.

8.5.8.1 Alternatively, the entire sampling system may be carried about by placing the pump in a camera bag or other suitable carrier with the inlet of the cartridge exposed.

8.5.8.2 An activity log should be maintained to show the monitored individual's location throughout the sampling period.

8.5.9 Record air temperature(s) and barometric pressure(s) periodically during the sampling period for correction of sampling data.

8.5.10 At the end of the sampling period, remove the cartridge, wrap with the original foil, and return to sealed, labeled containers for transport to the laboratory.

8.5.11 At least one field blank should be taken to the sampling site and returned to the laboratory with each group of samples.

9. Calibration of Pump

9.1 All air sampling pumps must be calibrated in the laboratory before use. For accurate calibration, attach the sampling cartridge in-line during calibration. Vinyl bubble tubing or other means (for example, rubber stopper or glass joint) may be used to connect the large end of the cartridge to the calibration system. Refer to Practice D 3686 or D 4185, Annexes on Methods for Calibration of Small Volume Air Pumps.

10. Sample Extraction Procedure

10.1 All samples should be extracted within one week after collection. If possible, samples should be stored at -10°C or below until analyzed.

10.2 Wash all glassware with laboratory detergent; rinse with deionized water, acetone, hexane, and again with deionized water; then fire in an oven (500°C). (**Warning**—Perform in a properly ventilated fume hood.)

10.3 Prepare a spiking solution for determination of extraction efficiency. The spiking solution should contain one or more surrogate compounds that have chemical structures and properties similar to those of the analytes of interest. Octachloronaphthalene and dibutylchlorodate have been used for determination of organochlorine pesticides by GC with electron capture detection. Tetrachloro-*m*-xylene and decachlorobiphenyl can be used together to ensure recovery of early and late eluting compounds. For organophosphate pesticides, tributylphosphate or triphenylphosphate may be employed. The