



Designation: D 4861 – 94a00

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 ~~describes~~ 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- $\mu\text{g}/\text{m}^3$ 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 ~~Notes 3~~ 10.24 and A1.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water²

¹ This practice is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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TABLE 1 Compounds for Which Procedure Has Been Tested

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

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

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 Standards—Methods~~⁵

EPA 600/4-89-017 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air^{5,6}

EPA-600/8-80-038 Manual

~~EPA 600/R-96/010b Compendium of Analytical Methods for Analysis of Pesticides the Determination to Toxic Organic Compounds in Humans Ambient Air~~

~~EPA 821/C-97-001 Methods and Environmental Samples~~⁵

² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol 11.03.

⁴ Annual Book of ASTM Standards, Vol 14.02.

⁵ Available from the U.S. Department Superintendent of Commerce, National Technical Information Service, Port Royal Road, Springfield, VA 22161; Documents, U.S. Government Printing Office, Washington, DC 20402.

⁶ Available from Noyes Data Corp., Park Ridge, NJ 07656.

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

EPA-600/4-90-010 Compendium Guidance for Analysis of Water

EPA SW-846 Test Methods for Determination of Air Pollutants in Indoor Air^{5,6}

EPA-600/4-88-039 Test Methods 515 and 531⁵ Evaluating Solid Waste Physical Chemical Methods

2.3 Other Document:

Code Government Standard:⁵

40 CFR 136 EPA Organic Chemical Analysis of Federal Regulations, Title 40, Part 136, Method 604⁷ 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 sampling efficiency, (dynamic retention efficiency) SE—ability of the sampling medium to trap vapors of interest. The percentage of retain the analyte of interest collected and retained by the sampling medium solution spike when it is introduced as a vapor in air or nitrogen into the air sampler and the sampler is operated drawn through the sampling cartridge under normal operating conditions and for a period the duration of the test period. The dynamic RE is normally equal to or greater less than that required for the intended use is indicated by % 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.

3.2.3 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.

3.2.4 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.

3.2.5 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.

3.2.6 relative retention time:

3.2.5 sampling efficiency, (RRTSE)—ratio—ability of RTs for two chemicals for the same chromatographic column sampling medium to trap vapors of interest. The percentage of the analyte of interest collected and carrier gas flow rate, where retained by the denominator represents 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):^{8,6} 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 electrolytic 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 retention times RTs during gas-liquid chromatography 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.

⁷ Available from Superintendent

⁷ Florisil is a trademark of Documents, U.S. Government Printing Office, Washington, DC 20402; the Floridin Corp., 5380 Capital Circle, N.W., Tallahassee, FL 32303. It is a natural magnesium silicate and is available from several commercial sources.

⁸ The boldface numbers in parentheses refer to the list of references at the end of this standard.

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

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. 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.



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

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

6.2 The ~~electron capture detector~~ 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—~~S~~ (see Fig. 1).

7.1.3 Sorbent, ~~polyurethane foam (PUF)~~, 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/cm^3 . 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 μm) 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 quartz microfiber micro-quartz-fibre, binderless, acid-washed filter (for example, Pallflex® Type 2500 QAT-UP^{11,9}) 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 1/16-in. (1.6-mm) diameter round perforations at 132 holes/in.² (20 holes/cm²), 41 % open area]. A 32-mm-V fluor elastomeric or polytetrafluoroethylene¹⁰ (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 an average particle-size cut-points of either 2.5 or 10 µm 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 sampler with a 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*, 1/2 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

⁸ Pallflex Products Corp., PO Box 929, Putnam, CT 06260.

⁹ "Tenax" is a registered trademark of the Enka, N.V., and is commercially available from several suppliers.

¹⁰ "Viton" is a registered trademark

¹⁰ Six percent and 10 % mixtures of the E. I. duPont de Nemours Co., Inc. diethyl ether in hexane have been used without apparent effect on method performance.

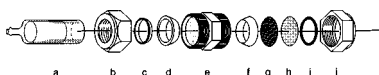


FIG. 2 Open-Face Filter Assembly: (a) Sampling Cartridge, (b) Inner Nut, (c) Back Ferrule, (d) Front Ferrule, (e) Union, (f) Front Ferrule, (g) Filter Support, (h) Filter, (i) Vi Fluoroelastomeric or PTFE O-ring, (j) Outer Nut

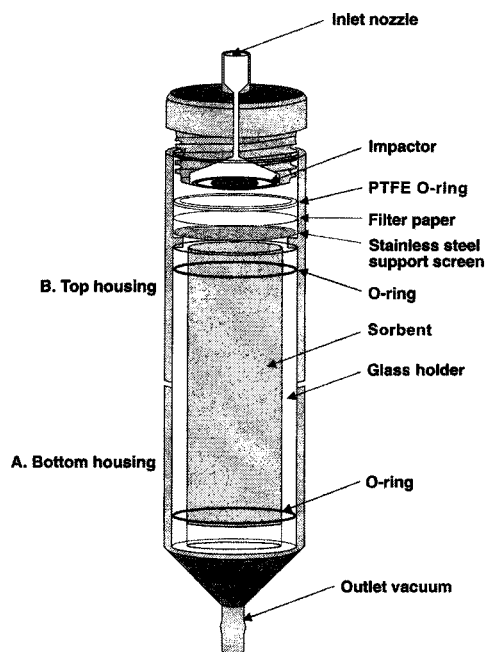


FIG. 3 Air Sampling Assembly with Size-selective Inlet, Particle Filter, and Glass Sorbent Cartridge

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.¹¹ 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 DB-5,¹² DB-17, DB-608, DB-1701

⁸ Florisil is a trademark

¹¹ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the Florida Corp., 5380 Capital Circle, N.W., Tallahassee, FL 32303; *American Chemical Society, see Anal. 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.

poly(5 %-diphenyl-95 %-dimethylsiloxane)¹², (50 %-phenyl)-methylpolysiloxane¹³ fused-silica, and others are commercially available.

7.5.3 *HPLC-e Column*, such as a ~~4.6-mm × 25-cm Zorbax SIL~~¹⁴ 4.6-mm × 15-cm reversed-phase octadecyldimethylsilane

¹² Currently

¹² This column is available from Supelco, Inc., Catalog No. 2-0557 or SKC, Inc., Catalog No. 226-92; several commercial sources under such trade names as DB-5, SPB-5, Rtx-5, HP-5, OV-5, BP-5, and others.

¹³ Swagelok® Part No. NY-1610-6 or equivalent, has been found satisfactory for this purpose.

¹³ 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.

(C-18) or ~~μBondapak C-18~~¹⁴ porous silica gel. Other columns may also provide acceptable results.

7.5.4 *Microsyringes*, 5- μ L 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^{-3-4} mm Hg. **kPa (41)**. A useful combination trap can be assembled by “sandwiching” 0.6 g of ~~Tenax-GC~~¹⁴ a sorbent, such as 2,6-diphenyl-*p*-phenylene oxide (Tenax)¹⁴ or styrene-divinylbenzene (XAD-2) polymer beads, between two 22-mm (diameter) \times 3.8-cm pre-cleaned PUF plugs, as shown in Fig. 1, Cartridge b. The ~~Tenax-GC~~ 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 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 ~~Aleonox~~¹⁵ laboratory detergent; rinse with deionized water, acetone, hexane, and again with deionized water; then fire in an oven (500°C).

~~NOTE 1~~ **Warning:** Perform (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 surrogate solution

should be prepared so that addition of 100 μL into the PUF plug results in an extract containing the surrogate compound at the high end of the instrument's calibration range.

10.4 Prepare 5 % diethyl ether in *n*-hexane¹⁵ by case lot of hexane. Remove 1900 mL of hexane from the freshly opened 1-gal bottle and add 100 mL of freshly opened ethyl ether (preserved with ethanol) to the flask.

10.5 Rinse condenser towers with 5 % diethyl ether/hexane.

10.6 Wipe off bench in hood with 5 % diethyl ether/hexane.

10.7 Add 300 mL of 5 % diethyl ether/hexane to 500-mL round bottom boiling flask and add up to three boiling granules.

10.8 Rinse a large sheet of aluminum foil with 5 % diethyl ether/hexane. Be sure to use waste rinse container. Place foil, rinsed side up, on bench for holding forceps and glassware. Rinse forceps with 5 % diethyl ether/hexane.

10.9 With gloved hands (see 7.2.13) remove sampling cartridge from jar and unwrap aluminum foil. Handle cartridge minimally, placing it on its own aluminum foil wrapping.

10.10 With pre-rinsed forceps, carefully remove the foam plug from the sampling cartridge and place in a 300-mL Soxhlet extractor.

NOTE 21—If “sandwich” trap is used, carefully clean outside walls of cartridge with hexane-soaked cotton swabs or laboratory tissues (discard) and place cartridge into extraction with intake (large end) downward.

10.11 Add 100 μL of spiking solution dropwise to the top of the PUF plug (or into the small of the glass cartridge).

10.12 Connect the Soxhlet extractor to the 500-mL boiling flask. Wet the joint with 5 % diethyl ether/hexane for a good seal. Place the forceps on the aluminum foil wrapping.

10.13 Taking the pre-rinsed forceps, adjust the PUF plug in the Soxhlet to wedge it midway along the length of the siphon. Rinse the inside of the glass sampling cartridge with 5 % diethyl ether/hexane into the Soxhlet. Place the forceps on the aluminum foil sheet. Dispose of the aluminum foil wrapping and place the glass cartridge aside for washing and recycling.

10.14 Connect the Soxhlet to the condenser, wetting the glass joint with 5 % diethyl ether/hexane for a good seal.

10.15 Repeat 10.9-10.14 for all samples, being sure to include a solvent blank and a control sample, if they exist.

10.16 Check water flow to condenser towers and turn on the heating unit.

10.17 As samples begin to boil, check Soxhlet extractors to make sure that they are filling and siphoning properly (4 to 6 cycles/h). Allow samples to cycle overnight or for a minimum of 16 h.

10.18 Turn off heating units and allow samples to cool to room temperature.

10.19 Set up Kuderna-Danish (K-D) concentrators with concentrator tubes. Rinse and add one boiling granule to each concentrator tube.

10.20 Pack lower ends of filter tubes with glass wool and fill each tube with anhydrous sodium sulfate to a depth of about 40 mm. Place the tube in the neck of K-D.

10.21 Carefully remove Soxhlet extractors and boiling flasks from condenser towers, and drain remaining solvent into each boiling flask.

10.22 Carefully pour each sample through a filter tube into K-D. Rinse each boiling flask three times with hexane, swirling hexane along sides of boiling flask. Once sample has drained, rinse down filter tube with hexane.

10.23 Attach each Snyder column to the K-D and rinse Snyder column to wet joint.

10.24 Place each K-D on steam bath and evaporate sample to approximately 5 mL.

NOTE 3—**Caution:** Do not let sample go to dryness.

10.25 Remove sample from steam bath and rinse Snyder column with a minimum of hexane. Allow sample to cool.

10.26 Adjust volume in concentrator tube to 10 mL, add glass stopper, and wrap joint with TFE-fluorocarbon tape. Alternatively, the sample may be quantitatively transferred (with rinsing of concentrator tube) to pre-scored vials and made to final volume.

10.27 Store concentrated extracts at -10°C or lower temperatures until analyzed. Analyze within two weeks of extraction.

11. Analysis Procedures

11.1 Analytical methods that have been used to determine various pesticides and PCBs collected from air by this procedure have been published ~~(10)~~(2).

11.1.1 Other methods for determination of pesticide and PCB residues that may be adapted to analysis of air samples may be found in EPA 821/C-97/001, 40 CFR 136, and EPA SW-846.

11.2 Organochlorine pesticides, PCBs, and many non-chlorinated pesticides are responsive to electron capture detection (see Table 1). Most of these compounds can be analyzed at concentrations of 1 to 50 ng/mL by GC/ECD. Reference methods include CFR 40.136 (EPA Method 608) and EPA SW 846. The following procedure is appropriate:

11.2.1 Select GC column (for example, 0.325-mm by 30-m-~~DB~~ poly-5 %-diphenyl-95 %-dimethylsiloxane column with 0.25 μm film thickness¹⁰) and appropriate GC conditions to separate the target analytes. Typical operating parameters for this column with splitless injection are: Carrier gas-chromatography grade helium at a flow rate of 1 to 2 mL/min and a column head pressure of 7 to 9 psi (48 to 60 kPa); injector temperature of 250°C ; detector temperature of 350°C ; initial oven temperature of 50°C , held for 2.0 min, ramped at $15^{\circ}\text{C}/\text{min}$ to 150°C for 8 min, ramped at $10^{\circ}\text{C}/\text{min}$ to 295°C then held for 5 min; purge time of 1.0 min. A typical injection volume is 2 to 3 μL .

11.2.2 Remove the sample extract from the freezer and allow to warm to room temperature.

11.2.3 Prepare standard solution from reference materials of known purity. Analytically pure standards of organochlorine pesticides and PCBs are available from several commercial sources.

11.2.4 Use the standard solutions of the various compounds of interest to determine ~~relative retention times (RRTs)~~ RRTs to an internal standard such as p,p'-DDE, aldrin, or octachloronaphthalene. Use 1 to 3- μ L injections or other appropriate volumes.

11.2.5 Determine detector linearity by injecting standard solutions of three different concentrations that bracket the required range of analyses.

11.2.6 Calibrate the system daily with a minimum of three injections of calibration standards.

11.2.7 Inject 1 to 3 μ L of sample extract using the solvent flush technique. (see appropriate paragraphs of Practice D 3687, Calculation Section). Record volume injected to the nearest 0.05 μ L.

11.2.8 If the response (peak height or area) exceeds the linear range of the detector, dilute the extract and reanalyze.

11.2.9 Quantify PCB mixtures by comparison of the total heights or areas of GC peaks with the corresponding peaks in the best-matching standard. Use Aroclor 1242 for early-eluting PCBs and either Aroclor 1254 or Aroclor 1260 as appropriate for late-eluting PCBs.

11.2.9.1 For specific congener analyses, all 209 PCB congeners are known to be separable by a combination of two capillary GC columns:

11.2.9.1.1 Column 1: 0.25-mm by 30-m poly(50 % *n*-octyl/50 % methylsiloxane), 0.25- μ m film thickness.¹⁶

11.2.9.1.2 Column 2: 0.25-mm by 30-m 100 % poly(dimethylpolysiloxane), 0.25- μ m film thickness.¹⁷

NOTE 2—Other GC columns may be substituted provided that PCBs 126 and 169 can be resolved from the most closely eluting congeners. The valley height between PCB 126 or 169 and its respective most closely eluting leading and trailing congeners must be less than 10 % of the height of the shorter of the pair. See Ref. (11) for examples of other columns and column pairs that have been found to be effective at resolving PCB congeners.

NOTE 3—Not all PCB congeners may be detectable with the relatively small air volume sampled by this method.

11.2.10 If both PCBs and organochlorine pesticides are present in the same sample, use column chromatographic separation on silicic acid in accordance with Refs (3) or (4) prior to GC analysis.

11.2.11 If polar compounds are present that interfere with GC/ECD analysis, use column chromatographic cleanup or alumina, activity grade IV, in accordance with Ref (2).

11.2.12 ~~For confirmation use, a second GC column such as DB-608.~~

~~11.2.13 For improved resolution use of slightly different polarity is recommended, especially when a capillary column such as an 0.25-mm (inside diameter) \times 30-m DB-5 with 0.25- μ m film thickness. The nonspecific detector is employed.~~

11.2.13 The following chromatographic conditions are appropriate GC/ECD analysis of organochlorine pesticides:

11.2.13.1 Helium carrier gas at 1 mL/min. Column temperature program, 90°C (4 min)/16°C/min to 154°C/4°C/min to 270°C. Detector, ⁶³Ni ECD at 350°C. Make up gas, nitrogen, or 5 % methane/95 % argon at 60 mL/min. Splitless injection, 2 μ L maximum. Injector temperature, 220°C.

11.2.14 Class separation and improved specificity can be achieved by column chromatographic separation on Florisil (4).

11.2.15 ~~A Hall electrolytic conductivity detector (HECD)~~ HECD operated in the reductive mode may be substituted for the electron capture detector for improved specificity. Sensitivity, however, will be reduced by at least an order of magnitude.

11.3 Organophosphorus pesticides are responsive to flame photometric and nitrogen-phosphorus (alkali flame ionization) detection. Most of these compounds can be analyzed at concentrations of 50 to 500 ng/mL using either of these detectors.

Reference methods include 40 CFR 136 (EPA Method 622) and EPA SW 846 (Method 8121).

11.3.1 Procedures given in 11.2.1-11.2.9 and 11.2.12-11.2.14 apply, except for the selection of surrogates.

11.3.2 Use tributylphosphate, triphenylphosphate, or other suitable compound(s) as surrogates to verify extraction efficiency and to determine RRTs.

11.4 Triazine, carbamate, and urea pesticides may be determined by capillary GC ~~(DB-5, DB-17, on nonpolar or DB-1701 stationary phase)~~ intermediate polarity phase columns, such as poly(5 %-diphenyl-95 %-dimethylsiloxane¹⁰, (35 %-phenyl)-methylpolysiloxane¹⁸, (50 %-phenyl)-methylpolysiloxane¹¹, or (14 %-cyanopropylphenyl)methylpolysiloxane¹⁹ columns, using nitrogen-phosphorus detection or MS-SIM with detection limits in the 0.05 to 0.2 μ g/mL range. Thermal degradation may be minimized by reducing the injector temperature to 200°C. HPLC may also be used, but detection limits will be higher (1 to 5 μ g/mL).

11.4.1 ~~*N*-Methyl carbamates may be determined using reverse-phase high-performance liquid chromatography (HPLC) (C-18) and HPLC on a C-18 (for example, 40 CFR 136 (EPA Method 632) or by HPLC with post-column derivatization w using *o*-phthaldehyde and fluorescence detection (for example, EPA Method 531.1, EPA 821/C-97/001, EPA SW 846 (Method 8318)).~~ Detection limits of 0.01 to 0.1 μ g/mL can be achieved.

¹⁶ University Research Glassware, PO Box 368, Corboro, NC 27510, Catalog No. URG-2000-25A, or equivalent.

¹⁶ This column is available under the trade name as SPB-Octyl.

¹⁷ Kontes Catalog No. K-570050, size 1025 or equivalent.

¹⁷ This column is available from several commercial sources under such trade names as DB-1, SPB-1, Rtx-1, HP-1, OV-1, BP-1, and others.

¹⁸ Kontes Catalog No. K-570050, size 0124 or equivalent.

¹⁸ This column is available from several commercial sources under such trade names as DB-35, SPB-35, Rtx-35, HP-35, and others.

¹⁹ Corning Catalog No. 9480 or equivalent.

¹⁹ This column is available from several commercial sources under such trade names as DB-1701, SPB-1701, HP-1701, OV-1701, Rtx-1701, and others.

11.5 Many urea pesticides, pyrethrins, phenols, and other polar pesticides may be analyzed successfully by GC/MS using polar column phases or after derivatization (12). Some polar pesticides require analysis by HPLC with fixed or variable wavelength UV detection (for example, EPA 821/C0-97/001, Method 1660, and EPA SW 846, Method 8325). Either reversed-phase or normal-phase chromatography may be used. Detection limits are 0.2 to 10 µg/mL of extract. An acceptable procedure is given as follows:

11.5.1 Select a suitable HPLC column (for example, ~~Zorbax-SH, 4.6-mm inside diameter × 25-cm, a bonded or µ-Bondapak C18, 3.9 mm × 30-cm, nonbonded, reversed-phase C18 or oxyldimeqthysilane [C8] or porous spherical silica gel column, 3.9 mm × 15 to 30 cm~~).

11.5.2 Select a suitable solvent system for the mobile phase (for example, mixtures of methanol or acetonitrile with water or mixtures of heptane or hexane with isopropanol). Mobile phases with phosphate or ammonium acetate buffers are often preferred.

11.5.3 Follow analytical procedures given in 11.1.2 through 11.1.9.

11.5.4 If interferences are present, adjust the HPLC solvent system composition or use column chromatographic clean-up with silica gel, alumina, or Florisil (4).

11.5.5 An electrochemical detector may be used to improve sensitivity for some ureas, carbamates, and phenolics. Much more care is required in using this detector, particularly in removing dissolved oxygen from the mobile phase and sample extracts.

11.5.6 Chlorophenols (di- through penta-) may be analyzed by GC/ECD or GC/MS after derivatization with pentafluorobenzylbromide (40 CFR 136, EPA Method 604).

11.5.7 Chlorinated phenoxyacetic acid herbicides and pentachlorophenol can be analyzed by GC/ECD or GC/MS after derivatization with diazomethane (EPA 821/C-97/001, Method 515.1). ~~DB-5~~ Poly(5 %-diphenyl-95 %-dimethylsiloxane)¹⁰ and DBF-170† (14 %-cyanopropylphenyl)methylpolysiloxane¹⁷ columns (0.25-mm inside diameter × 30-m) at 60 to 300°C/4°C per min have been found to perform well. Pentafluorobenzylation followed by GC/ECD or GC/MS has also been successfully applied to the determination of acid herbicides (for example, EPA SW 846, Method 8151A).

11.6 A mass spectrometer operating in full-scanning mode is useful for confirmation and identification of pesticides. A mass spectrometer operating in selected-ion monitoring (SIM) mode can be used as a sensitive detector for multi-residue determination of a wide variety of pesticides. ~~Mass spectrometers are now available that provide detection limits comparable to nitrogen-phosphorous and electron-capture detectors. pesticides.~~

11.6.1 Most of the pesticides shown in Table 1 have been successfully determined by GC/MS-SIM. Typical GC-operating parameters are as described in 11.2.1.

11.6.1.1 Examples of GS/MS methods that have been successfully applied to multiresidue pesticide and PCB analyses may be found in Ref. 12; 40 CFR 136, EPA Methods 525.2, 625, and 1625; EPA SW 846, Methods 8270 and 8275A; and elsewhere.

11.6.2 The mass spectrometer is typically operated using positive ion electron impact ionization (70 eV). Other instrumental parameters are instrument specific.

11.6.3 *p*-Terphenyl-d₁₄ is commonly used as a surrogate for GC/MS analysis.

11.6.4 Quantification is typically performed using an internal standard method. 1,4-Dichlorobenzene, naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂ are commonly used as internal standards.

11.7 See Practice D 3687 for solvent-flush injection technique, determination of relative retention times, and other procedures pertinent to GC and HPLC analyses.

11.8 If concentrations are too low to detect by the analytical procedure of choice, the extract may be concentrated to 1 mL or 0.5 mL by carefully controlled evaporation under an inert atmosphere. The following procedure is appropriate:

11.8.1 Place K-D concentrator tube in a water bath and analytical evaporator (nitrogen blow-down) apparatus. The water bath temperature should be from 25 to 50°C.

11.8.2 Adjust nitrogen flow through hypodermic needle to provide a gentle stream.

11.8.3 Carefully lower hypodermic needle into the concentrator tube to a distance of about 1 cm above the liquid level.

11.8.4 Continue to adjust needle placement as liquid level decreases.

11.8.5 Reduce volume to slightly below desired level.

11.8.6 Adjust to final volume by carefully rinsing needle tip and concentrator tube well with solvent (usually *n*-hexane).

12. Calculation

12.1 Determination of Concentration:

12.1.1 The concentration of the analyte in the extract solution can be taken from a standard curve where peak height or area is plotted linearly against concentration in nanograms per millilitre (ng/mL).

12.1.2 From the standard curve, determine the nanograms of analyte standard equivalent to the peak height or area for a particular compound.

12.1.3 Ascertain whether the field blank has been contaminated. Blank levels should not exceed 10 ng/sample for organochlorine pesticides or 100 ng/sample for PCBs and other pesticides. If the blank has been contaminated, the sampling series must be held suspect. (See appropriate paragraph in Practice D 3686, Section on Sampling with Activated Charcoal Samplers.)

12.1.4 The quantity of compound in the sample is calculated using the following equation:

$$A = 1000 \left(\frac{A_s \times V_e}{V_i} \right) \quad (1)$$

where:

- A = amount of analyte in the sample, ng,
 A_s = calculated amount of material injected onto the chromatograph based on calibration curve for injected standard, ng,
 V_e = final volume of extract, mL,
 V_i = volume of extract injected, μL , and
 1000 = factor required for conversion of microlitres to millilitres.

12.1.5 The extraction efficiency (EE) is determined from the recovery of the surrogate spike as follows:

$$EE(\%) = \frac{S}{S_a} \times 100 \quad (2)$$

where:

- S = amount of spike recovered, ng, and
 S_a = amount of spike added to plug, ng.

12.1.6 The total amount in nanograms found in the sample is corrected for extraction efficiency and laboratory blank as follows:

$$A_c = \frac{A - A_o}{EE(\%)} \quad (3)$$

where:

- A_c = corrected amount of analyte in sample, ng, and
 A_o = amount of analyte in blank, ng.

12.1.7 Determine the total volume of air sampled under ambient conditions using the following equation:

$$V_a = \frac{\sum_{i=1}^n (T_i \times F_i)}{1000 \text{ L/m}^3} \quad (4)$$

where:

- V_a = total volume of air sampled, m^3 ,
 T_i = length of sampling segment between flow checks, min, and
 F_i = average flow during sampling segment, L/min.

12.1.8 Correct the air volume to 25°C and 760 mm Hg (STP) as follows:

$$V_s = V_a \left(\frac{P_b - P_w}{760 \text{ mm Hg}} \right) \times \left(\frac{298 \text{ K}}{T_a} \right) \quad (5)$$

where:

- V_s = volume of air at standard conditions, m^3 ,
 P_b = average ambient barometric pressure, mm Hg,
 P_w = vapor pressure of water at calibration temperature, mm Hg, and
 T_a = average ambient temperature, K .

12.1.9 If the criteria for a proper sample have been met, calculate the concentration, C_a , of compound in nanograms per cubic metre (ng/m^3) of air as follows:

$$C_a = \frac{A_c}{V_s} \times \frac{100}{SE(\%)} \quad (6)$$

where:

SE = sampling efficiency as determined by the procedure outlined in Annex A1.

12.1.10 If it is desired to convert the air concentration value to parts per trillion (ppt) (wt/wt) in dry air at STP:

$$\text{ppt} = 0.844 C_a \quad (7)$$

12.1.11 To convert the air concentration to parts per trillion (pptv) (v/v) in air at STP:

$$\text{pptv} = \frac{24.45 C_a}{MW} \quad (8)$$

where:

MW = molecular weight of the compound of interest.

12.1.12 If quantification is performed using an internal standard, a relative response factor (RRF) is calculated by the equation:

$$RRF = I_s C_{is} / I_{is} C_s \quad (9)$$

where:

- I_s = integrated area of the target analyte peak,
 I_{is} = integrated area of the internal standard peak, and

C_s = concentration of the internal standard.

12.1.13 The concentration of the analyte (C_x) in the sample is then calculated as follows:

$$C_x = I_x / RRF \quad (10)$$

where:

I_x = integrated area of the target analyte peak, and

RRF = relative response factor.

13. Sensitivity of the Procedure

13.1 Several different parameters involved in both the sampling and analysis steps of this practice collectively determine the sensitivity with which each compound is detected. As the volume of air sampled is increased, the sensitivity of detection increases proportionately within limits set by: (a) the retention efficiency for each specific component trapped on the ~~polyurethane foam~~ PUF plug and (b) the background interference associated with the analysis of each specific component at a given site sampled. The sensitivity of detection of samples recovered by extraction depends on: (a) the inherent response of the particular GC detector used in the determinative step and (b) the extent to which the sample is concentrated for analysis. It is the responsibility of the analyst(s) performing the sampling and analysis steps to adjust parameters so that the required detection limits can be obtained.

14. Precision and Bias

14.1 Precision and bias in this type of analytical procedure are dependent upon the precision and bias of the analytical procedure for each compound of concern, and the precision and bias of the sampling process.

14.2 The reproducibility of this method for most compounds for which it has been evaluated ranges from ± 5 to ± 30 % (measured as the relative standard deviation) when replicate sampling cartridges are used ($N > 5$). Sample recoveries for individual compounds generally fall within the range from 90 to 110 %, but recoveries ranging from 65 to 125 % are considered acceptable. Use of PUF alone may result in lower recoveries for more volatile compounds (for example, those with saturation vapor pressures $> 10^{-3}$ mm Hg; $> 10^{-4}$ kPa). In those cases, another sorbent or a combination of PUF and Tenax GC (see Cartridge b, Fig. 1) should be employed.

14.3 Sampling efficiency and precision data for a group of common pesticides, PCBs, and other semivolatile organic chemicals are given in Tables X1.1-X2.2.

15. Keywords

15.1 air; Aroclors; carbamates; chlorophenols; chlorophenoxy acids; organochlorines; organophosphates; PCBs; pesticides; polychlorinated biphenyls; polyurethane foam; pyrethrins; sampling and analysis; semivolatile organics; triazines; ureas

ANNEX

(Mandatory Information)

A1. DETERMINATION OF SAMPLING EFFICIENCY AND SPIKE RECOVERY

A1.1 Before using this procedure the user should determine the sampling efficiency for the compound of interest. The sampling efficiencies shown in Appendix X1 were determined for approximately 1 m^3 of air at about 25°C , sampled at 3.8 L/min. Sampling efficiencies for the pesticides shown in Appendix X2 are for 24 h at 3.8 L/min and 25°C . For compounds not listed, longer sampling times, different flow rates, or other air temperatures, the following procedure may be used to determine sampling efficiencies:

A1.1.1 Assemble apparatus as shown in Fig. A1.1.

A1.1.2 Place clean PUF in pre-filter and attach inlet to nitrogen line. Alternatively, the entire assembly may be placed in a nitrogen-filled glove box or isolation ~~chamber~~.

~~NOTE A1.1—Warning: Clean chamber.~~ (Warning—Clean nitrogen should be used instead of air to prevent oxidation of the compounds under test. Such oxidation, if it should occur, would not necessarily reflect what might be encountered during actual sampling and may give misleading results as to sampling efficiencies.)

A1.1.3 Place 22-mm \times 7.6-cm PUF plugs in the primary and secondary trays and attach to the pump.

A1.1.4 Prepare a standard solution of the compound of interest in a volatile solvent such as hexane, pentane, or benzene.

A1.1.5 Place a small, accurately measured volume (for example, 1 mL) of standard solution into the modified Midget impinger.

A1.1.6 Set pump at the sampling rate that will be used in field application.

A1.1.7 Start the pump and draw nitrogen through the assembly for a period of time equal to or exceeding that intended for field application.

A1.1.8 Remove PUF plugs and analyze separately in accordance with the procedure in Sections 10 and 11.

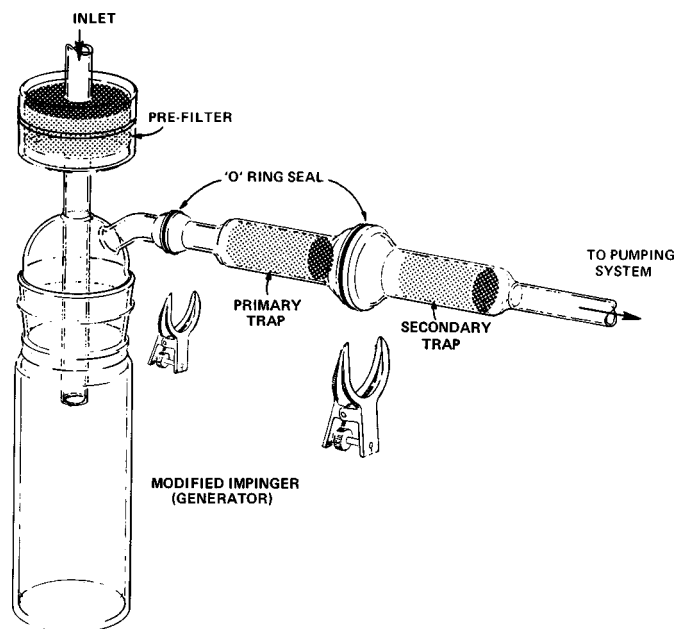


FIG. A1.1 Apparatus for Determining Sampling Efficiencies

A1.1.9 Rinse impinger with hexane or other suitable solvent and quantitatively transfer to volumetric flask or concentrator tube for analysis.

A1.1.10 Determine the sampling efficiency using the following equation:

$$\% SE = \left(\frac{W_1}{W_o - W_r} \right) \times 100 \quad (A1.1)$$

where:

- W_o = original amount of compound added to the impinger,
- W_r = residue left in the impinger at the end of the test, and
- W_1 = amount of compound extracted from the primary trap.

A1.1.11 If material is found in the secondary trap, it is an indication that breakthrough has occurred. The addition of the amount found in the secondary trap, W_2 , to W_1 will provide an indication of the overall sampling efficiency of a tandem-trap sampling system.

A1.1.12 The sum of W_1 , W_2 (if any), and W_r must equal W_o or the test is invalid.

A1.1.13 If the compound of interest is not sufficiently volatile to vaporize at room temperature, the impinger may be heated in a water bath or other suitable heater to a maximum of 50°C to aid volatilization.

A1.1.14 If the compound of interest cannot be vaporized at 50°C or without thermal degradation, dynamic retention efficiency (RE_d) may be used to estimate sampling efficiency. Retention efficiency RE determination may be made in the following manner:

A1.1.14.1 Spike a pair of PUF plugs by slow, dropwise addition of the standard solution (see A1.1.4) to the one end of each plug. Use no more than 0.5 to 1 mL of solution. Amounts added to each plug should be as nearly the same as possible.

A1.1.14.2 Allow the plug to dry for 2 h in a clean, protected place (for example, desiccator).

A1.1.14.3 Place one spiked plug in the primary trap so that the spiked end is at the intake and place a clean, unspiked plug in the secondary trap.

A1.1.14.4 Wrap the other spiked plug in hexane-rinsed aluminum foil and store in a clean place for the duration of the test. This is the static control plug.

A1.1.14.5 Draw pre-filtered nitrogen or ambient air through the assembly in accordance with A1.1.6 and A1.1.7.

NOTE A1.21—Impinger may be discarded.

A1.1.14.6 Separately analyze each PUF plug in accordance with the procedure in Sections 10 and 11.

A1.1.14.7 Calculate % RE_d as follows:

$$\% RE_d = \frac{W_1}{W_o} \times 100 \quad (A1.2)$$

where:

- W_o = amount of compound added to primary plug, and
- W_1 = amount of compound recovered from primary plug.

A1.1.14.8 If a residue, W_2 , is found on the secondary plug, breakthrough has occurred.

A1.1.14.9 The sum of $W_1 + W_2$ must equal W_o within $\pm 25\%$ or the test is invalid.

A1.1.14.10 For most compounds tested by this procedure % RE_d values are generally less than % SE values determined as in A1.1.

A1.1.14.11 The purpose of the static RE_d determination is to establish any loss or gain of analyte unrelated to the flow of nitrogen or air through the PUF plug.

APPENDIXES

(Nonmandatory Information)

X1. SAMPLING AND RETENTION EFFICIENCY DATA FOR SEVERAL CLASSES OF PESTICIDES AND OTHER SEMIVOLATILE ORGANIC CHEMICALS

X1.1 The data shown in Tables X1.1-X1.4 were determined using the procedure in Annex A1 (1, 6). Sampling rates were 3.8 L/min and sampling times were generally 4 h. Sampling volumes were generally 0.9 m³. In the case of the 2,4-D esters shown in Table X1.1, the sampling time was 16 h, providing for a 3.6-m³ air sample.

TABLE X1.1 Sampling Efficiencies for Some Organochlorine Pesticides

Compound	Quantity Introduced, µg	Air Volume, m ³	Sampling Efficiency, %		<i>n</i>
			mean	RSD	
α-Hexachlorocyclohexane (α-BHC)	0.005	0.9	115	8	6
γ-Hexachlorocyclohexane (Lindane)	0.05–1.0	0.9	91.5	8	5
Chlovidane, technical	0.2	0.9	84.0	11	8
<i>p,p'</i> -DDT	0.6, 1.2	0.9	97.5	21	12
<i>p,p'</i> -DDE	0.2, 0.4	0.9	102	11	12
Mirex	0.6, 1.2	0.9	85.9	22	7
2,4-D Esters:					
isopropyl	0.5	3.6	92.0	5	12
butyl	0.5	3.6	82.0	10	11
isobutyl	0.5	3.6	79.0	20	12
isooctyl	0.5	3.6	>80 ^A

^A Not vaporized. Value based on % RE = 81.0 (RSD = 10 %, *n* = 6).

TABLE X1.2 Sampling Efficiencies for Some Semivolatile Organochlorine Compounds and PCBs

Compound	Quantity Introduced, ^A µg	Sampling Efficiency, %		<i>n</i>
		mean	RSD	
1,2,3-Trichlorobenzene	1.0	6.6 ^B	22	8
1,2,3,4-Tetrachlorobenzene	1.0	62.3 ^B	33	5
Pentachlorobenzene	1.0	94.0	12	5
Hexachlorobenzene	0.5, 1.0	94.5	8	5
Hexachlorocyclopentadiene	1.0	8.3 ^B	12	5
2,4,5-Trichlorophenol	1.0	108	3	5
Pentachlorophenol	1.0	107	16	5
Aroclor 1242	0.1	96.0	15	6
Aroclor 1254	0.1	95.0	7	6
Aroclor 1260	0.1	109	5	11

^A Air volume = 0.9 m³.

^B % SEs were 98, 98, and 97 % (*n* = 2), respectively, for these three compounds by the PUF/Tenax® GC "Sandwich" trap.

TABLE X1.3 Sampling Efficiencies for Organophosphorus Pesticides

Compound	Quantity Introduced, ^A µg	Sampling Efficiency,%		n
		mean	RSD	
Dichlorvos (DDVP)	0.2	72.0	13	2
Ronnel	0.2	106	8	12
Chlorpyrifos	0.2	108	9	12
Diazinon	1.0	84.0	18	18
Methyl parathion	0.6	80.0	19	18
Ethyl parathion	0.3	75.9	15	18
Malathion	0.3	100 ^B

^A Air volume = 0.9 m³.

^B Decomposed in generator; value based on % RE = 101 (RSD = 7, n = 4).

TABLE X1.4 Sampling Efficiencies for Carbamates, Ureas, Triazines, and Pyrethrins

Compound	Spike Level, ^A µg/plug	Static Recovery, %		n	Retention Efficiency, %		n	Sampling Efficiency, %		n
		mean	RSD		mean	RSD		mean	RSD	
Carbamates										
Propoxur	5	61.4	10	6	77.6	37	6	96.7	11	6
Carbofuran	15	55.3	12	6	64.2	46	6	87.2	14	6
Bendicarb	50	57.3	11	6	69.8	43	6	62.1	14	6
Mexacarbate	10	62.8	19	6	62.7	41	6	89.8	14	6
Carbaryl	100	56.6	14	6	63.6	53	6	^B	13	6
Ureas:										
Monuron	19	87.0	6	6	91.2	6	5	^C		
Diuron	20	84.1	8	6	90.0	2	5	^C		
Linuron	20	86.7	8	6	92.5	4	5	^C		
Terbutiuron	18	85.0	8	6	88.8	8	5	^C		
Fluometuron	20	91.4	10	6	101	3	5	^C		
Chlortoluron	20	86.2	11	6	92.0	7	5	^C		
Triazines:										
—Simazine	—40	403—	—6	5	404—	—9	6	^C		
—Atrazine	—10	404—	—7	5	—98.9	—7	6	^C		
—Propazine	—40	—405	44	5	—99.9	44	6	^C		
—Simazine	—10	103	6	5	101	9	6	^C		
—Atrazine	—10	104	7	5	98.9	7	6	^C		
—Propazine	—10	105	11	5	99.9	14	6	^C		
Pyrethrins:										
Pyrethrin I	(9.7) ^D	90.5	10	6	95.6	22	5	^C		
Pyrethrin II	(6.1) ^D	88.6	11	6	69.9	29	5	^C		
Allethrin	25	69.2	9	5	58.3	12	6	^C		
<i>d-trans</i> -Allethrin	25	76.8	9	6	74.4	9	5	^C		
Dicrotophos	25	72.0	22	6	71.7	8	5	^C		
Resmethrin	25	76.5	14	6	66.7	14	6	^C		
Fenvalerate	25	87.9	3	6	57.2	20	3	^C		

^A Air volume = 0.9 m³.

^B Decomposed in generator.

^C Not vaporized.

^D Estimated on the basis of 20 µg Pyrethrin with a composition of 48.4 % and 30.3 % by weight of Pyrethrins I and II, respectively.

X2. SAMPLING AND RETENTION EFFICIENCY DATA FOR SEVERAL PESTICIDES OVER 24-H SAMPLING PERIODS

X2.1 The data shown in Tables X2.1 and X2.2 were determined in accordance with the procedure in Annex A1 (102). The sampling rate was 3.8 L/min and the sampling time was 24 h, providing for a sampling volume of 5.5 m³.

TABLE X2.1 Extraction and 24-H Sampling Efficiencies for Various Pesticides and Related Compounds

Compound	Extraction Efficiency, ^A %		Sampling Efficiency, ^B %, at					
			10 ng/m ³		100 ng/m ³		1000 ng/m ³	
	mean	RSD	mean	RSD	mean	RSD	mean	RSD
Chlorpyrifos	83.3	11.5	83.7	18.0	92.7	15.1	83.7	18.0
Pentachlorophenol	84.0	22.6	66.7	42.2	52.3	36.2	66.7	42.2
Chlordane	95.0	7.1	96.0	1.4	74.0	8.5	96.0	1.4
<i>o</i> -Phenylphenol	47.0	46.7	46.0	19.1	45.3	29.9	46.0	19.1
Lindane	96.0	6.9	91.7	11.6	93.0	2.6	91.7	11.6
DDVP	88.3	20.2	51.0	53.7	106.0	1.4	51.0	53.7
2,4-D methyl ester	75.3	6.8	58.0	23.6	75.3	6.8
Heptachlor	99.0	1.7	97.3	13.6	103.0	17.3	97.3	13.6
Aldrin	97.7	4.0	90.7	5.5	94.0	2.6	90.7	5.5
Dieldrin	95.0	7.0	82.7	7.6	85.0	11.5	82.7	7.6
Ronnel	80.3	19.5	74.7	12.1	60.7	15.5	74.7	12.2
Diazinon	72.0	21.8	63.7	18.9	41.3	26.6	63.7	19.9
<i>trans</i> -Nonachlor	97.7	4.0	96.7	4.2	101.7	15.3	96.7	4.2
Oxychlordane	100.0	0.0	95.3	9.5	94.3	1.2	95.3	9.5
α -BHC	98.0	3.5	86.7	13.7	97.0	18.2	86.7	13.7
Bendiocarb	81.3	8.4	59.7	16.9	30.7	23.5	59.7	16.9
Chlorothalonil	90.3	8.4	76.7	6.1	70.3	6.5	76.7	6.1
Heptachlor epoxide	100.0	0.0	95.3	5.5	97.7	14.2	95.3	5.5
Dacthal	87.0	9.5	95.3	22.2	87.0	9.5
Aroclor 1242	91.7	14.4	95.0	15.5	94.7	17.5	95.0	15.5

^A Mean values for one spike at 550 ng/plug and two spikes at 5500 ng/plug.

^B Mean values for three determinations.

TABLE X2.2 Extraction and 24-H Dynamic Retention Efficiencies for Various Pesticides and Related Compounds

Compound	Extraction Efficiency, ^A %		Sampling Efficiency, ^B %, at					
			10 ng/m ³		100 ng/m ³		1000 ng/m ³	
	mean	RSD	mean	RSD	mean	RSD	mean	RSD
Propoxur	77.5	71.4	92.0	...	91.7	22.8	101.0	18.4
Resmethrin	95.5	71.4	79.0	...	100.7	13.1	107.0	4.4
Dicofol	57.0	8.5	38.0	25.9	65.0	8.7	69.0	...
Captan	73.0	12.7	56.0	...	45.5	64.3	84.3	16.3
Carbaryl	74.0	82.0	102.0	...	61.0	...	113.0	6.1
Malathion	76.5	44.5	108.0	...	54.0	16.0	77.3	7.6
<i>cis</i> -Permethrin	88.7	10.3	101.0	28.5	85.0	26.9	89.0	11.3
<i>trans</i> -Permethrin	88.7	11.0	67.3	34.8	80.7	56.4	108.3	9.5
Methoxychlor	65.5	4.9	78.5	2.1
Atrazine	75.0	50.5	73.0	30.1	83.0	9.5
Folpet	86.7	11.7	78.0	...	93.0	...
Aroclor 1260	92.0	14.5	88.0	9.6	85.3	9.9	107.7	13.6

^A Mean values for one spike at 550 ng/plug and two spikes at 5500 ng/plug.

^B Mean values for generally three determinations.

X3. STORAGE STABILITIES FOR VARIOUS PESTICIDES AND OTHER COMPOUNDS ON POLYURETHANE FOAM

X3.1 If possible, sampling cartridge should be stored at water ice or dry ice temperatures immediately after collection in the field and for no longer than 30 days at -10°C or lower in a laboratory freezer before they are analyzed. The data presented in Table X3.1 show storage stabilities for 30 days at room temperature (1). Table X3.2 gives similar data obtained under very adverse conditions; for example, when wrapped only in aluminum foil and stored in the trunk of an automobile in an unshaded parking lot when the average maximum daytime temperature was 32°C .

TABLE X3.1 Storage Stability of Spiked^A PUF Cartridges Stored at Room Temperature (24°C) for 30 Days

Compound	% Recovered		
	mean	RSD	<i>n</i>
Chlorpyrifos	100.0	18.3	3
Pentachlorophenol	103.7	47.6	3
Chlordane	97.7	4.0	3
<i>o</i> -Phenylphenol	61.7	10.4	3
Lindane	100.3	12.9	3
DDVP	62.0	29.5	3
Heptachlor	129.0	26.0	3
Aldrin	104.3	9.7	3
Dieldrin	103.7	11.6	3
Ronnel	26.0	11.4	3
Diazinon	74.0	6.1	3
<i>trans</i> -Nonachlor	118.3	16.3	3
Oxychlordane	97.0	4.4	3
α -BHC	106.3	18.8	3
Bendiocarb	86.7	3.2	3
Chlorothalonil	46.7	9.6	3
Heptachlor epoxide	123.3	17.4	3
Propoxur	87.7	2.5	3
Resmethrin	81.0	9.2	3
Dicofol	54.3	21.4	3
Captan	124.7	23.7	3
Carbaryl	88.0	1.7	3
Malathion	13.7	4.5	3
<i>cis</i> -Permethrin	84.3	33.2	3
<i>trans</i> -Permethrin	84.5	41.7	2
Methoxychlor	100.0	9.6	3
Atrazine	74.7	7.4	3
Folpet	58.5	57.3	2
Aroclor 1242	99.3	5.5	3
Aroclor 1260	100.3	6.5	3

^A Spiked at 5.5 μ g/plug.

TABLE X3.2 Storage Stabilities of Spiked PUF Cartridges Under Very Adverse Conditions^A

Compound	% Recovered					
	Day 0			Day 15		
	mean	RSD	<i>n</i>	mean	RSD	<i>n</i>
α -BHC	90	10	6	87	28	6
β -BHC	86	30	6
Lindane	100	6	4	89	29	6
Heptachlor	78	13	6
Endosulfan I	117	19	6
Mirex	89	1	4	116	17	6
1,3,5-Trichlorobenzene	57	18	6
1,2,3,4-Tetrachlorobenzene	88	7	4	76	12	6
Pentachlorobenzene	93	6	4	78	15	6
Pentachloronitrobenzene	87	16	6
Dichlorvos	70	12	3	4	187	6
Ronnel	91	9	3	56	13	6
Chlorpyrifos	89	4	3	76	13	6
Diazinon	79	10	8	101	15	6
Methyl parathion	80	14	8	76	13	6
Ethyl parathion	80	14	8	88	11	6

^A Stored wrapped in aluminum foil in an automobile trunk. Average daily maximum temperature 32°C.

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