This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: D4861 – 23

Standard Practice for Sampling and Selection of Analytical Techniques for Pesticides and Polychlorinated Biphenyls in Air[1]

This standard is issued under the fixed designation D4861; 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 air for a variety of common pesticides and polychlorinated biphenyls (PCBs) and provides guidance on the selection of appropriate analytical measurement methods. Other compounds such as polychlorinated dibenzodioxins/furans, polybrominated biphenyls, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons, and polychlorinated naphthalenes may be efficiently collected from air by this practice, but guidance on their analytical determination is not covered by this practice.

1.2 The sampling and analysis of PCBs in air can be more complicated than sampling PCBs in solid media (for example, soils, building materials) or liquids (for example, transformer fluids). PCBs in solid or liquid material are typically analyzed using Aroclor[2] distillation groups in chromatograms. In contrast, recent research has shown that analysis of PCBs in air samples by GC-ECD has also been found to exhibit potential uncertainties due to changes in the PCB patterns, differences in responses in distillation groups, peak co-elutions and differences in response factors within a homolog group (**1, 2**).[3] As such it is recommended that PCBs in air not be quantified using AroclorTM distillation groups. In addition, it is recommended that analysis of PCBs in air be done using GC-MS rather than GC-ECD. Any mention, to outdated practices for "Aroclor" and GC-ECD analysis of PCBs herein are retained solely for historical perspective.

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

1.4 This practice is based on the collection of chemicals from air onto polyurethane foam (PUF) or a combination of PUF and granular sorbent (for example, diphenyl oxide, styrene-divinylbenzene), or a granular sorbent alone.

1.5 This practice is applicable to multicomponent atmospheres, 0.001 μg/m^3 to 50 μg/m^3 concentrations, and 4 h to 24 h sampling periods. The limit of detection will depend on the nature of the analyte and the length of the sampling period.

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

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazards statements, see 10.24 and A1.1.

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[4]

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)

D3687 Test Method for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method

D4185 Test Method for Measurement of Metals in Workplace Atmospheres by Flame Atomic Absorption Spectrophotometry

[1] This practice is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

Current edition approved Sept. 1, 2023. Published September 2023. Originally approved in 1991. Last previous edition approved in 2017 as D4861 – 17 which was withdrawn September 2021 and reinstated in September 2023. DOI: 10.1520/D4861-23.

[2] A trade name formerly used by Monsanto Corporation, Creve Coeur, MO.

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

[4] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Copyright © ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. United States

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
Chlorobiphenyl Congeners or Homologs	GC-MS	Hexachlorocyclopentadiene[B,C]	GC-ECD or MS
		Lindane (γ-HCH)	GC-ECD
		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	*trans*-Nonachlor	GC-ECD or MS
Cholorotoluron	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	Pentachlorobenzine	GC-ECD or MS
2,4-D, acid, esters and salts	GC-ECD or MS[D]	Pentachlorphenol	GC-ECD or MS
Dacthal	GC-ECD or MS	Permethrin (*cis* and *trans*)	GC-MS
p,p'-DDT	GC-ECD or MS	*o*-Phenylphenol	HPLC-UV, GC-ECD, or MS
p,p'-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	Terbuthiuron	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/2,6-diphenyl-*p*-phenylene oxide "sandwich" trap.
[C] Compound is very unstable in solution.
[D] Derivatization necessary for free acid and salts.

iTeh Standards
(https://standards.iteh.ai)
Document Preview
ASTM D4861-23
https://standards.iteh.ai/catalog/standards/sist/580e57de-6f2d-41ed-8d4d-614270acd982/astm-d4861-23

E355 Practice for Gas Chromatography Terms and Relationships

2.2 *EPA Methods and Standards:*

EPA 600/R-96/010b Compendium of Methods for the Determination to Toxic Organic Compounds in Ambient Air[5]

EPA 821/C-99-004 Methods and Guidance for Analysis of Water, Versions 2[6]

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

40 CFR 136 EPA Organic Chemical Analysis of Municipal and Industrial Wastewater[7]

2.3 *NIOSH Methods:*[8]

NIOSH Manual of Analytical Methods

NOTE 1—ASTM does not recommend NIOSH 5503 for PCB analysis due to Aroclor quantitation and GC-ECD analysis.

3. Terminology

3.1 *Definitions*—Refer to Terminology D1356 and Practice E355 for definitions of terms used in this practice.

3.2 *Definitions of Terms Specific to This Standard:*

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

3.2.4 *retention time,* (RT)*, n*—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)*, n*—ability of the sampling medium to trap vapors of interest; the percentage of the analyte

[5] Also available at http://www.epa.gov/ttnamti1/files/ambient/airtox/tocomp99.pdf
[6] NTIS PB99-500209 (see http://www.ntis.gov/products/epa-water-methods.aspx)
[7] Also available at http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&tpl=/ecfrbrowse/Title40/40cfr136_main_02.tpl
[8] Also available at http://www.cdc.gov/niosh/docs/2003-154/

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, n*—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 L/min to 5 L/min) sampler is used to collect vapors on a sorbent cartridge containing PUF or PUF in combination with another solid sorbent, or another solid sorbent alone. Airborne particles may also be collected, but the sampling efficiency is not known. The method is adopted from Ref (**3**) 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. For PCBs, MS detection is the recommended detector with congener or homolog based quantitation.

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, or by mass spectrometric analysis.

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. Interferences

6.1 Any gas or liquid chromatographic separation of complex mixtures of organic chemicals is subject to serious interference problems due to coelutions 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. The analysis of PCBs in air samples by GC-ECD is not recommended.

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 (**4**).

6.5.2 PCBs may be separated from organochlorine pesticides by column chromatography on silicic acid. See Refs (**5**) and (**6**).

6.5.3 Many pesticides can be fractionated into groups by column chromatography on Florisil[9] (**6**).

7. Apparatus

7.1 *Air Sampler:*

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

7.1.2 *Sampling Cartridge,* constructed from a 20 mm (inside diameter) by 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/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:

[9] Florisil is a trademark of the U.S Silica Co., Berkeley Springs, WV. It is a natural magnesium silicate and is available from several commercial suppliers.

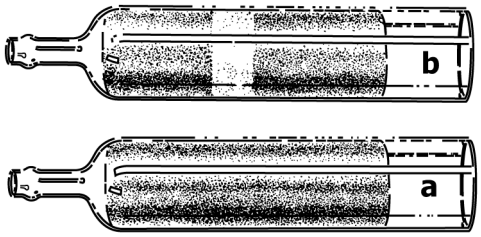

FIG. 1 PUF Sampling Cartridge (a) and PUF "Sandwich" Sampling Cartridge (b)

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. Other combinations (that is, PUF/solid sorbent/PUF or solid sorbents only, with glass, polymer or metal cartridge casings) may also be used.

7.1.5 *Particle Filter,* if desired, may be utilized. The collection efficiency of PUF for small-diameter (0.1 µm to 1 µm) airborne particles is only about 20 % (**7**). However, most pesticides and PCBs exist in air under steady-state conditions, primarily as vapors (**8**). Most particulate-associated pesticides or PCBs, if any, will also tend to be vaporized from filters after collection (**9**). 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 (**10**).

7.1.5.1 An open-face filter may be attached to the sampling cartridge by means of a union for 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, 0.8 mm thick with 1.6 mm diameter round perforations at 20 holes/cm^2, 41 % open area). A 32 mm fluoroelastomeric or polytetrafluoroethylene (PTFE) O-ring is placed between the filter and outer nut to affect a seal (see Fig. 2).

7.1.6 *Size-Selective Impactor Inlet* with particle-size cut-points of either 2.5 µm or 10 µm mean diameter at a sampling rate of 4 L/min may be used to exclude non-respirable airborne particulate matter (**11, 12**). 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,* 14 mm,

7.2.7 *Filter Tubes,* size 40 mm (inside diameter) by 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 quality,[10]

7.2.18 *n-Hexane,* pesticide quality,[10]

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 D1193.

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.

[10] Glass distilled and certified for pesticides analysis by GC-ECD.

[11] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

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

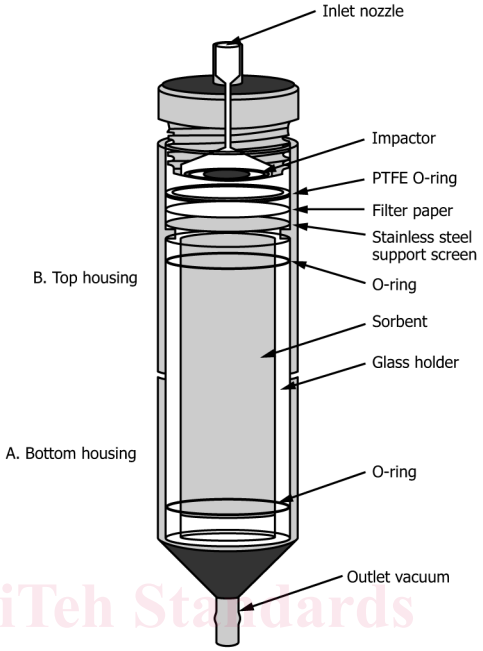

FIG. 3 Air Sampling Assembly with Size-selective Inlet, Particle Filter, and Glass Sorbent Cartridge

iTeh Standards
(https://standards.iteh.ai)
Document Preview
ASTM D4861-23
https://standards.iteh.ai/catalog/standards/sist/e5fde-6f3d-41ed-8d4d-614270acd982/astm-d4861-23

7.5.2 *Gas Chromatographic Columns,* such as a 0.25 mm or 0.32 mm (inside diameter) by 30 m poly(5 %-diphenyl-95 %-dimethylsiloxane),[12] (50 %-phenyl)-methylpolysilozane[13] fused-silica, and others are commercially available.

7.5.3 *HPLC Column,* such as a 4.6 mm by 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 h to 24 h at 4 cycles/h 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 h 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 (**3**). A useful combination trap can be assembled by "sandwiching" a layer of granular polymeric sorbent, such as 2,6-diphenyl-*p*-phenylene oxide or styrene-divinylbenzene polymer beads, between two 22 mm (diameter) by 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 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.

[12] 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.

[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.

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 m 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 D3686 or D4185, 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 tap water, followed with deionized water, then with a suitable pesticide-quality solvent such as acetone or methanol. Dry in a vacuum oven or explosion-proof convection oven. (**Warning—**If an unvented oven is used, 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 dibutylchlorendate 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*-hexane[14] by case lot of hexane. Remove 1900 mL of hexane from the freshly opened 4 L 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. If the "sandwich" trap is used, carefully clean outside walls of cartridge with cotton swabs or laboratory tissues, wetted with hexane or other suitable pesticide-quality solvent (discard the wipes—do not add to sample extract), before placing the cartridge into the extractor. If cartridge Type B (Fig. 1) is used, place it with the intake (large end) downward.

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

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.

[14] Six percent and 10 % mixtures of diethyl ether in hexane have been used without apparent effect on method performance.

10.17 As samples begin to boil, check Soxhlet extractors to make sure that they are filling and siphoning properly (4 cycles/h 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.

NOTE 2—Microprocessor-controlled concentrators that provide automated sample evaporation under mild thermal conditions (for example, TurboVap[15]) may be used in place of K-D concentrators.

NOTE 3—Rotary evaporators may be used if the user is careful to assure that the flask does not approach dryness and that a suitable recovery surrogate with a vapor pressure equal to or higher than that of the most volatile target analytes is added prior to concentration.

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. (**Warning—**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, if possible. If longer storage times are necessary, sample should be frozen (–20 °C or lower).

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 (**4**, **13**). The analysis of PCBs in air samples by GC-ECD is not recommended and other methodologies (see 11.2.9) are recommended.

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 (for example, 680, 1668c), and EPA SW-846 (for example, 8270).

11.2 Organochlorine pesticides, PCBs, and many nonchlorinated pesticides are responsive to electron capture detection (see Table 1). Most of these compounds can be analyzed at concentrations of 1 ng/mL to 50 ng/mL by GC-ECD. Reference methods include 40 CFR 136 (EPA Methods 608 and 625) and EPA SW 846. The following procedure is generally appropriate:

NOTE 4—Analysis by GC-MS is the recommended analytical method for PCBs in air samples.

11.2.1 Select GC column (for example, 0.25 mm by 30 m poly-5 %-diphenyl-95 %-dimethylsiloxane column with 0.25 µm film thickness[12]) 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 mL/min to 2 mL/min and a column head pressure of 48 kPa 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 °C/min to 150 °C for 8 min, ramped at 10 °C/min to 295 °C then held for 5 min; purge time of 1.0 min. A typical injection volume is 2 µL 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 congeners are available from several commercial sources.

11.2.4 Use the standard solutions of the various organochlorine compounds of interest to determine RRTs to an internal standard such as octachloronaphthalene. Use 1 µL to 3 µL 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 µL to 3 µL of sample extract using the solvent flush technique. (see appropriate paragraphs of Practice D3687, Calculation Section). Record volume injected to the nearest 0.05 µL.

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 PCBs in air samples using GC-MS on a congener or homolog specific basis (**1**, **2**, **14**, **15**, **16**).

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:

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

(2) Column 2: 0.25 mm by 30 m 100 % poly(dimethylpolysiloxane), 0.25 µm film thickness.[17]

[15] The sole source of supply of the apparatus known to the committee at this time is MABiotage AB, Uppsala, Sweden, http://www.biotage.com. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee [1], which you may attend.

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

[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.