



Designation: D4861 – 23

# Standard Practice for Sampling and Selection of Analytical Techniques for Pesticides and Polychlorinated Biphenyls in Air<sup>1</sup>

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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 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<sup>2</sup> 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).<sup>3</sup> As such it is recommended that PCBs in air not be quantified using Aroclor<sup>TM</sup> 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 Any mention, to outdated practices for “Aroclor” and GC-ECD analysis of PCBs herein are retained solely for historical perspective.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  $\mu\text{g}/\text{m}^3$  to 50  $\mu\text{g}/\text{m}^3$  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:*<sup>4</sup>

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

<sup>1</sup> 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.

<sup>2</sup> A trade name formerly used by Monsanto Corporation, Creve Coeur, MO.

<sup>3</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

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

**TABLE 1 Compounds for Which Procedure Has Been Tested**

Compound	Recommended Analysis <sup>A</sup>	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 <sup>B,C</sup>	GC-ECD or MS
		Lindane ( $\gamma$ -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 ( $\alpha$ - and $\beta$ -Hexachlorocyclohexanes)	GC-ECD or MS	Methoxychlor	GC-ECD or MS
Captan	GC-ECD or MS	Metolachlor	GC-ECD or MS
Carbaryl	HPLC-UV or GC-MS	Mexacarbate	
Carbofuran	HPLC-UV or GC-MS	Mirex	GC-ECD or MS
Chlordane, technical	GC-ECD or MS	Monuron	HPLC-UV
Chlorothalonil	GC-ECD or MS	<i>trans</i> -Nonachlor	GC-ECD or MS
Chlorotoluron	HPLC-UV or GC-MS	Oxychlordan	GC-ECD or MS
Chlorpyrifos	GC-ECD or MS	Parathion	GC-NPD, FPD, or MS
Cyfluthrin	GC-ECD or MS	Pentachlorobenzene	GC-ECD or MS
2,4-D, acid, esters and salts	GC-ECD or MS <sup>D</sup>	Pentachlorophenol	GC-ECD or MS
Dacthal	GC-ECD or MS	Permethrin ( <i>cis</i> and <i>trans</i> )	GC-MS
<i>p,p'</i> -DDT	GC-ECD or MS	<i>o</i> -Phenylphenol	HPLC-UV, GC-ECD, or MS
<i>p,p'</i> -DDE	GC-ECD or MS	Phorate	GC-NPD, FPD, or MS
Diazinon	GC-NPD, FPD, or MS	Propazine	GC-NPD or MS
Dicloran	GC-ECD or MS	Propoxur (Baygon)	GC-NPD or MS
Dieldrin	GC-ECD or MS	Pyrethrin	GC-MS
Dichlorvos (DDVP)	GC-ECD or MS	Resmethrin	GC-MS
Dicofol	GC-ECD or MS	Ronnel	GC-ECD or MS
Dicrotophos	HPLC-UV or GC-MS	Simazine	HPLC-UV or GC-MS
Diuron	HPLC-UV or GC-MS	Terbutiuron	HPLC-UV or GC-MS
Endrin	GC-ECD or MS	1,2,3,4-Tetrachlorobenzene <sup>B</sup>	GC-ECD or MS
Fenvalerate	HPLC-UV or GC-MS	1,2,3-Trichlorobenzene <sup>B</sup>	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

<sup>A</sup> 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.)

<sup>B</sup> Using PUF/2,6-diphenyl-*p*-phenylene oxide "sandwich" trap.

<sup>C</sup> Compound is very unstable in solution.

<sup>D</sup> Derivatization necessary for free acid and salts.

### 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](#)<sup>5</sup>

[EPA 821/C-99-004 Methods and Guidance for Analysis of Water, Versions 2](#)<sup>6</sup>

[EPA SW-846 Test Methods for Evaluating Solid Waste Physical Chemical Methods](#)

[40 CFR 136 EPA Organic Chemical Analysis of Municipal and Industrial Wastewater](#)<sup>7</sup>

#### 2.3 NIOSH Methods:<sup>8</sup>

[NIOSH Manual of Analytical Methods](#)

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

<sup>5</sup> Also available at <http://www.epa.gov/ttnamti1/files/ambient/airtox/tocomp99.pdf>

<sup>6</sup> NTIS PB99-500209 (see <http://www.ntis.gov/products/epa-water-methods.aspx>)

<sup>7</sup> Also available at [http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&tpl=/ecfrbrowse/Title40/40cfr136\\_main\\_02.tpl](http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&tpl=/ecfrbrowse/Title40/40cfr136_main_02.tpl)

<sup>8</sup> Also available at <http://www.cdc.gov/niosh/docs/2003-154/>

### 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

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<sup>9</sup> (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 ( $\leq \pm 5\%$ ) 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<sup>3</sup>. 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:

<sup>9</sup> 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.