Designation: D 6160 – 98 (Reapproved 2003)ε1

An American National Standard

Standard Test Method for Determination of Polychlorinated Biphenyls (PCBs) in Waste Materials by Gas Chromatography[1]

This standard is issued under the fixed designation D 6160; 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.

ε[1] NOTE—Warning notes were editorially moved into the standard text in August 2003.

1. Scope

1.1 This test method[2] is a two-tiered analytical approach to PCB screening and quantitation of liquid and solid wastes, such as oils, sludges, aqueous solutions, and other waste matrices.

1.2 Tier I is designed to screen samples rapidly for the presence of PCBs.

1.3 Tier II is used to determine the concentration of PCBs, typically in the range of from 2 to 50 mg/kg. PCB concentrations greater than 50 mg/kg are determined through analysis of sample dilutions.

1.4 This is a pattern recognition approach, which does *not* take into account individual congeners that might occur, such as in reaction by-products. This test method describes the use of Aroclors[3] 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, and 1268, as reference standards, but others could also be included. Aroclors 1016 and 1242 have similar capillary gas chromatography (GC) patterns. Interferences or weathering are especially problematic with Aroclors 1016, 1232, and 1242 and may make distinction between the three difficult.

1.5 This test method provides sample clean up and instrumental conditions necessary for the determination of Aroclors. Gas chromatography (GC) using capillary column separation technique and electron capture detector (ECD) are described. Other detectors, such as atomic emission detector (AED) and mass spectrometry (MS), may be used if sufficient performance (for example, sensitivity) is demonstrated. Further details about the use of GC and ECD are provided in Practices E 355, E 697, and E 1510.

1.6 Quantitative results are reported on the dry weights of waste samples.

1.7 Quantification limits will vary depending on the type of waste stream being analyzed.

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 and health practices and determine the applicability of regulator limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 4059 Test Method for Analysis of Polychlorinated Biphenyls in Insulating Liquids by Gas Chromatography[4]

E 203 Test Method for Water Using Karl Fischer Titration[5]

E 288 Specification for Laboratory Glass Volumetric Flasks[6]

E 355 Practice for Gas Chromatography Terms and Relationships[7]

E 697 Practice for Use of Electron-capture Detectors in Gas Chromatography[7]

E 969 Specification for Glass Volumetric (Transfer) Pipet[6]

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatography[7]

2.2 *U.S. EPA Standards:*

Method 608 Organochlorine Pesticides and PCBs[8]

Method 680 Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry[9]

Method 3620 Florisil Column Clean-Up[10]

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

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[2] This test method is based largely on EPA 8080 (and the proposed modification for the use of capillary columns, EPA 8081) and EPA Report 600/4–81–045 by Bellar, T. and J. Lichtenberg, reported in 1981. The report is titled,“ The Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils” and provides significant support to the protocol below.

[3] Aroclor Standards may be purchased as 1000 µg/mL in *iso*octane. Aroclor is a registered trademark of Monsanto.

[4] *ASTM Annual Book of Standards*, Vol 10.03.

[5] *ASTM Annual Book of Standards*, Vol 15.05.

[6] *ASTM Annual Book of Standards*, Vol 14.04.

[7] *Annual Book of ASTM Standards*, Vol 03.06.

[8] EPA Report 600/4/82–057, Environmental Monitoring and Support Laboratory, Cincinnati, OH.

[9] Alford-Stevens, Ann, et al, Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory Office of Research and Development, USEPA, Cincinnati, OH.

[10] U.S. EPA, “Test Methods for Evaluating Solid Waste,” *Physical/Chemical Methods*, SW-846.

Method 3630 Silica Gel Clean-Up[10]
Method 3660 Sulfur Clean-Up[10]
Method 8082 Determination of PCB in Water and Soil/Sediment by Gas Chromatography: Capillary Column Technique[10]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *Aroclors*, *n*—commercial mixtures of polychlorinated biphenyl congeners marketed and trademarked by Monsanto prior to 1977.

3.1.1.1 *Discussion*—Specific Aroclors are usually designated by a four-digit number, with the first two digits usually designating the number of carbon atoms and the last two digits providing the chlorine content (for example, Aroclor 1260 is 60 % (weight) chlorine).

3.1.2 *congeners*, *n*—compounds related by structural similarities.

3.1.2.1 *Discussion*—All polychlorinated biphenyls (PCBs) share the same C_{12} structure and vary only by the number and position of the chlorine atoms attached to the aromatic rings.

3.1.3 *continuing calibration standard (CCS)*—a known blend or one or more Aroclors at a fixed concentration that is injected into the gas chromatograph to demonstrate the validity of the calibration.

3.1.4 *dry weight*, *n*—concentration of PCBs after factoring out the water content.

3.1.4.1 *Discussion*—This correction assumes that all PCBs originated from nonaqueous sources and any water present has been added subsequently, diluting the original concentration. This correction can be described using the formula:

$$\text{Aroclor (mg/Kg) (dry)} = \frac{\text{Aroclor (mg/Kg) (wet)}}{(100 - \%\ \text{water})/100} \quad (1)$$

3.1.5 *instrument performance standard (IPS)*, *n*—a known low level of an Aroclor in a clean solvent used as a comparator to determine which qualitative (screening) results are of sufficient magnitude to require quantitative analyses.

3.1.6 *surrogate*, *n*—compound or compounds that are similar to analytes of interest in chemical composition, extraction, and chromatography, but that are not normally found at significant levels in the matrices of interest.

3.1.6.1 *Discussion*—Surrogates may be spiked into blanks, standards, samples, or matrix spikes prior to analysis to allow a determination of a quantitative recovery rate. Surrogates are also used to document matrix effects and method control.

3.1.7 *waste material*, *n*—any matter, within the scope of this test method, that is in the process of being recycled or disposed.

4. Summary of Test Method

4.1 The sample is extracted with solvent and the extract is treated to remove interfering substances, if needed. The sample extract is injected into a gas chromatograph. The components are separated as they pass through the capillary column and polychlorinated biphenyl compounds, if present, are detected by an ECD.

NOTE 1—Portions of this test method are similar to EPA Methods 608, 680, and 8082.

4.2 For screening (Tier I), instrument performance is monitored by a 2-µL injection of a standard containing Aroclors 1016 and 1260. For low level work (1 ppm) the instrument is checked with a standard concentration of 0.01 µg/mL (each) and for higher level work (10 ppm), the instrument is checked with a 0.1 µg/mL standard.

4.3 Identification involves a pattern comparison of the chromatograms of an unknown sample with that of a standard obtained under identical instrumental conditions.

4.4 When quantification is required (Tier II), an external standards method (ESTD) is used. The quantitation technique typically requires a comparison of five peaks (minimum of three) between the chromatograms of an unknown sample and that of standard Aroclor obtained under identical conditions. Quantitation of either Aroclors 1016 or 1260 is performed using a five-point calibration of a mixed Aroclor standard containing Aroclors 1016 and 1260. All remaining Aroclors are quantitated from single point calibrations. Calibration is verified daily by comparison of results obtained for analysis of the midpoint calibration standard of Aroclor 1016 and 1260 to the five-point calibration curve. (See Appendix X1 for an example chromatogram and calibration table.)

5. Significance and Use

5.1 This test method provides sufficient PCB data for many regulatory requirements. While the most common regulatory level is 50 ppm (dry weight corrected), lower limits are used in some locations. Since sensitivities will vary for different types of samples, one shall demonstrate a sufficient method detection limit for the matrix of interest.

5.2 This test method differs from Test Method D 4059 in that it provides for more sample clean-up options, utilizes a capillary column for better pattern recognition and interference discrimination, and includes both a qualitative screening and a quantitative results option.

6. Interferences

6.1 The ECD has selective sensitivity to alkyl halides, conjugated carbonyls, nitrogen compounds, organometallics, and sulfur. Therefore, the chromatogram obtained for each sample shall be carefully compared to chromatograms of standards to allow proper interpretation.

6.2 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts or interferences, or both, to standard analysis. All these materials shall be demonstrated to be free from interferences under the conditions of analysis by analyzing method blanks.

6.3 Interferences from phthalate esters may pose a major problem in Aroclor determinations when using ECD. Phthalates generally appear in the chromatogram as broad late eluting peaks. Since phthalates are commonly used as plasticizers and are easily extracted from plastic, all contact of samples and extracts with plastic should be avoided.

6.4 While general clean-up techniques are provided as part of this test method, some samples may require additional clean-up beyond the scope of this test method before proper instrumental analysis may be performed.

7. Apparatus

7.1 *Gas Chromatograph*, a temperature programmable gas chromatograph suitable for splitless injections; equipped with an ECD.

7.2 *Data System*, a data system capable of measuring peak areas.

7.3 *Regulator (Make-up Gas)*—N_2 or Ar:Methane (95:5); two stage regulator rated at 20 MPa (3000 psi) inlet and 35 to 860 kPa (5 to 125 psi) outlet.

7.4 *Regulator (Carrier Gas)*—H_2, two-stage regulator rated at 20 MPa (3000 psi) inlet and 35 to 860 kPa (5 to 125 psi) outlet.

7.5 *Gas Purifiers*, to remove moisture and particulates. Depending on the levels and types of interferences encountered, these might involve molecular sieves (moisture), activated carbon (organics), or other commercially-available media.

7.6 *Flow Meter*, to measure gas flow. Typical range is from 0.5 to 50 mL/min. ± 0.1 mL/min.

7.7 *Column*, crosslinked 5 % phenyl methyl silicone, 30 m by 0.32 mm id by 0.25 µm film thickness.

7.7.1 It is possible that other columns will provide sufficient separating power, but this shall be demonstrated before use.

7.8 *Analytical Balance*, capable of weighing to 0.0001 g.

7.9 *Volumetric Flasks*, 10, 50, 100, 200 mL, (see Specification E 288) Class A with ground-glass stoppers.

7.10 *Vortex Mixer*:

7.11 *Vials*, glass, 20 mL and 40 mL capacity with TFE-fluorocarbon-lined caps.

7.12 *Septum Inserts*—Inserts shall be treated with a silynization reagent before use or after cleaning. (See Annex A2 for possible procedure.) They may be purchased already treated.

7.13 *Volumetric Pipette*, 1, 5, 10 mL (see Specification E 969), Class A.

7.14 *Syringe*, 500 µL, mechanical guide.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents 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 first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Acetone*—(**Warning—**Extremely flammable. Vapors may cause flash fire.)

8.3 *Activated Magnesium Silicate (Florisil)*, Pesticide residue (PR) grade (60/100 mesh); store in glass containers with ground glass stoppers or foil lined screw caps.

8.3.1 Just before use, activate each batch at least 4 h at 130°C in a glass container loosely covered with aluminum foil. Alternatively, store the magnesium silicate in an oven at 130°C. Cool the magnesium silicate in a desiccator for 30 min before use.

8.4 *Hexane*—(**Warning—**Extremely flammable. Harmful if inhaled. May produce nerve cell damage. Vapors may cause flash fire.)

8.5 *Isooctane*—(**Warning—**Extremely flammable. Harmful if inhaled. Vapors may cause flash fire.)

8.6 *Methanol*—(**Warning—**Flammable. Vapor harmful. May be fatal or cause blindness if swallowed or inhaled. Cannot be made nonpoisonous.)

8.7 *Silynization Reagent* (for example, 5 % dimethyldichlorosilane in toluene). See Annex A2 for instructions.

8.8 *Sodium Sulfate*, granular, anhydrous (maintained at 130°C for at least 24 h prior to use). Cool the sodium sulfate in a desiccator for 30 min before use.

8.9 *Sulfuric Acid (concentrated)*:

8.10 *Acetone/Hexane*, 10 % acetone/90 % hexane (v/v).

8.11 *Gases*, Hydrogen (zero grade; 99.995 % purity) and nitrogen (zero grade; 99.998 % purity) or argon/methane (95:5; ECD grade).

8.11.1 Care shall be given to ensure purity of the carrier gas. For example, an in-line filter may be required.

8.12 *Aroclor Standards*[3], Aroclor 1016, 1221, 1232, 1242, 1254, 1260, 1262, 1268.

8.13 *Decachlorobiphenyl (DCB) (surrogate) Optional*:

8.13.1 *Surrogate Stock Standard (15 µg/mL) Preparation*—Accurately dilute 1.5 mL of 1000 µg/mL DCB concentrate in 100 mL volumetric flask and fill to the mark with methanol, yielding a 15 µg/mL solution.

8.13.2 *Surrogate Working Standard (1.5 µg/mL) Preparation*—Accurately dilute 10 mL of the 15 µg/mL DCB stock standard in a 100 mL volumetric flask and fill to the mark with methanol, yielding a 1.5 µg/mL working DCB standard.

NOTE 2—Sample preparations will normally use 0.1 mL of this solution. The resulting concentration in the sample extract is 0.005 µg/mL before any further dilutions. The following calculations show this.

$$1.5\ \mu g/mL \times 0.1\ mL = 0.15\ \mu g$$
$$\frac{0.15\ \mu g}{(3.0\ mL\ sample + 27\ mL)} = 0.005\ \mu g/mL \quad (2)$$

8.14 *Calibration Standards*:

8.14.1 *Intermediate Stock Standard (50 µg/mL)*:

If high level standards (for example, commercially available standards at 2000 to 5000 µg/mL) have been purchased, prepare solutions of 50 µg/mL concentration.

8.14.1.1 The surrogate calibration standard may be added (optional) to the Aroclor 1016/1260 intermediate stock standard at a concentration of 2.5 µg/mL. For preparation of the standard, add 500 µL of 50 µg/mL surrogate to a 10 mL volumetric flask containing 3.0 mL of *iso*octane. Add the Aroclor 1016/1260 standard (5.0 mL at 100 µg/mL) to the flask. Dilute to 10 mL volume with *iso*octane and mix well.

8.14.1.2 To prepare the continuing CCS, dilute 200 µL of the intermediate stock standard to 100 mL.

[11] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual 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.

Volume add into the 100 mL flask	Ar-1016/1260 concentration µg/mL	Surrogate concentration µg/mL
200 µL	0.10	0.005

8.14.2 *Instrument Performance Standard (IPS) (Tier I–Screening)*—An *iso*octane solution of Aroclors 1016 and 1260 is prepared at a concentration of 0.01 µg/mL (each) or 0.1 µg/mL (each) (depending on whether the minimum level of interest is 2 µg/mL or 20 µg/mL) from the appropriate stock standard.

8.14.2.1 If the surrogate (decachlorobiphenyl, (DCB)) is used, it shall be added to the IPS to result in a concentration of 0.005 µg/mL.

8.14.2.2 To prepare the IPS along with DCB, add 10 mL of Aroclor 1016/1260 at 0.1 µg/mL and 0.033 mL of DCB at 15 µg/mL into 100 mL volumetric flask. Dilute to 100 mL volume with *iso*octane. Mix well. This yields 0.01 µg/mL IPS and 0.005 µg/mL of DCB.

8.14.2.3 The following additional standards shall be run once (at 0.1 µg/mL) to demonstrate the Aroclor patterns and be mixed if preferred.

Aroclor	Mix with the following:
1268	1221 or 1232 or 1242 or 1248 or 1254
1262	1221 or 1232 or 1242 or 1248
1254	1221

8.14.3 *Individual Working Standards (Tier 2–Quantitation)*—Working standards are typically prepared in *iso*octane at concentrations of 0.02 µg/mL, 0.05 µg/mL, 0.1 µg/mL, 0.3 µg/mL and 0.5 µg/mL for Aroclors 1016 and 1260. All other Aroclors are prepared at the mid level concentration (0.1 µg/mL) for the single point calibration. An alternative calibration range may be used as long as the criteria for linearity of the calibration range is documented.

8.14.3.1 Aroclors 1016 and 1260 shall be a mixed standard. The following additional standards shall be run once (at 0.1 µg/mL) to demonstrate the Aroclor patterns and may be mixed, if preferred.

Aroclor	May be mixed with:
1268	1221 or 1232 or 1242 or 1248 or 1254
1262	1221 or 1232 or 1242 or 1248
1254	1221

8.15 *Quality Control Standards*:

8.15.1 *Calibration Check Standard (CCS) (Tier 2–Quantitation)*—This standard contains 0.1 µg/mL (those who are interested in the 20 mg/Kg level with no compositing, use 0.2 µg/mL each) each of Aroclors 1016 and 1260 in hexane.

8.15.1.1 The surrogate concentration, if used, is 0.005 µg/mL.

8.15.1.2 *Example*—To prepare the CCS along with DCB, add 20 mL of Aroclors 1016/1260 to 0.5 µg/mL and 0.05 mL of DCB at 10 µg/mL into 100 mL volumetric flask. Dilute to 100 mL volume with *iso*octane. Mix well. This yields a 0.1 µg/mL of CSS and 0.005 µg/mL of DCB.

8.15.2 *Matrix Spiking Standard (Tier 2–Quantitation)*—The matrix spiking standard is to contain Aroclor 1268 at a concentration of 50 µg/mL in methanol. Laboratories working at lower calibration ranges will need to dilute this (for example, to 25 µg/mL).

8.16 *Copper Powder*, 200 mesh, 99 % min..

8.17 *Silica Gel*, 100 to 200 mesh.

9. Sampling

9.1 PCBs are hydrophobic compounds. Therefore, when sampling, all organic phases, including bottom sludge beneath aqueous phases, shall be sampled. Given the possible presence of alcohols and glycols, it is typically not acceptable to sample the organic phase only.

9.2 Headspace above stored standards and samples or extracts should be minimized such that the volume is less than 50 %.

9.3 Three mL of sample are required for each determination. No special sample preservation is required other than storage in a closed container with minimal headspace. It is accepted practice to use borosilicate glass containers with TFE-fluorocarbon-lined lids.

10. Preparation of Apparatus

10.1 *General Gas Chromatographic Conditions*—The first temperature profile (12 min run time) is used for Tier I screening method for the presence of Aroclor. The longer second temperature profile (17 min run time) is used for Tier II to quantitate the Aroclors present, but may also be used for Tier I, if desired.

10.1.1 *Rapid Screen Capillary Column Oven Temperature Profile (Tier I, 12 min run time)*:

Initial value	130°C
Initial time	2 min
Program rate	20°C/min
Final value	270°C
Final time	3 min
Carrier gas	hydrogen
Head pressure	depend on DCB RT (approximately 105 KPa (15 psi)) column flow: 3.1-3.2 mL/min
Make-up gas	nitrogen or argon: methane
Make-up gas rate	approximately 65 mL/min.
Splitless mode	
Purge off	0 min
Purge on	1.0 min
Purge vent	2.5 mL/min
Split vent	50 mL/min
Sample injection	2.0 µL
Injector inlet system	250°C
Detector	315°C

10.1.2 *Quantitation Capillary Column Oven Temperature Profile (Tier II, 17 min run time; may also be used for Tier I analysis*:

Initial value	125°C
Initial time	3 min
Level I	
Program rate	12°C/min
Final value	270°C
Final time	2 min
Carrier gas	hydrogen
Head pressure	Depend on DCB RT (approximately, 105 KPa (15 psi))
Column flow	3.1 mL/min (approximately at 270°C)
Make-up gas	nitrogen
Make-up gas rate	approximately 65 mL/min
Splitless mode	
Purge off	0 min
Purge on	1.0 min

Purge rate	50 mL/min
Sample injection	2.0 µL
Injector inlet system	250°C
Detector	315°C

11. Calibration and Standardization

11.1 *Calibration*:

11.1.1 *Tier 1–Screening Method*—Aroclors are multi-peak chemical mixtures that have very unique identification patterns. All Aroclors shall be run individually or in mixtures at 0.1 µg/mL on each channel performing screening to produce reference patterns. It is important to note that some of these patterns have the same constituents and that some Aroclors are quantitated using the same peaks (such as Aroclors 1016 and 1232 or 1242). When screening for Aroclors, a visual determination is made by the following key items:

11.1.1.1 Aroclor pattern—(a) same singlets, doublets, and triplets present in the reference chromatograms, and (b) same relative peak heights between peaks in the sample chromatogram and the reference chromatogram.

11.1.1.2 Retention time shifts should be very consistent between the standard and the sample peaks.

11.1.1.3 All samples in which an Aroclor is detected (using Tier I) require a judgment concerning the amount. The recognized Aroclor pattern shall be compared to the IPS (0.01 µg/mL or 0.1 µg/mL). If the overall level of the suspected Aroclor pattern is equal to or greater than overall level of the IPS pattern, then Tier II analysis may be used to quantitate the sample. If multiple Aroclors are suspected, a Tier II analysis may be run to help resolve the mixture.

11.1.1.4 Recovery control limits for the surrogate are 40 to 150 % recovered. If the recovery is outside of these limits, see Annex A1.

11.1.2 *Tier I Calibration Check*—An instrument performance standard (IPS) at 0.01 µg/mL of Aroclor 1016 and 1260 is used to check the instrument sensitivity *once a day or every 20 samples, whichever is more frequent* (typically laboratories using ten samples compositing shall use the 0.01 µg/mL standard to achieve a detection limit of 5 µg/mL of Aroclor in any individual sample). Sample results will be compared qualitatively with the daily IPS. (See the Calculation section 13).

11.1.2.1 Tabulate the sum of the areas or the data system calculated amount of the five major peaks for each of the Aroclors 1016 ad 1260 in the instrument performance standard. The response shall be within 50 % of the initial response. Initial response shall be established by averaging the response of a minimum of five injections of the instrument performance standard (IPS). If the limit is exceeded, new limits may need to be established.

11.1.2.2 Likewise, the expected response for the surrogate, if used, is established by averaging the areas of DCB in the five initial IPS analyses.

11.1.2.3 The surrogate also may be used for retention time control. It is recommended that column flow be adjusted so DCB elutes between 10.5 to 11.5 min using the 12 min GC program. (This will typically require a column head pressure of 105 to 112 kPa.) (Alternatively, the retention time should be 15 to 16.5 min using the 17 min program.)

11.1.3 *Tier 2–Quantitative Method*—The GC data system must be calibrated for both Aroclors 1016 and 1260, using five peaks for each Aroclor. [For example, when using an integrator, divide the standard amount by the number of peaks being used. Using five peaks on a 0.5 µg/mL standard would assign 0.1 µg/mL to each peak. This will allow for a calibration table to be made, yielding response factors for each peak at the five levels of calibration. Set up a calibration table in the method file of the integrator or data system that is to be used. Calculate an average response factor for each of five peaks for both Aroclors. Calculate the standard deviation of the average response factor for each peak of the Aroclor using the following calculation.

$$S = \sqrt{\sum_{i=1}^{n} \frac{(X_i - X)^2}{n - 1}} \quad (3)$$

where:

S = standard deviation,
X_i = each observed value,
X = the arithmetic mean of observed values, and
n = total number of calibration points.

11.1.3.1 Calculate the percent relative standard deviations (% RSDs) for the response factors of the calibrated peaks for each Aroclor from the formula below. The acceptance criteria for the % RSD for each Aroclor is ≤20 %. If the average % RSD is greater than 20 % for either Aroclor, then linearity over the desired calibration range for that instrument has not been demonstrated.

NOTE 3—The % RSD is 100 % multiplied by the result of Eq 3 (s) divided by the arithmetic mean (X).

11.1.3.2 When samples are to be analyzed, instrument control is verified by analyzing the CCS and the percent difference (% D) is calculated. *The acceptance criteria is within +30 % for each AROCLOR in the CCS (1016 and 1260).*

11.1.3.3 If either Aroclor 1016 or 1260 is out of control for the daily CCS, corrective action shall be taken and a CCS reanalyzed. If corrective action does not correct the problem, then a new five point calibration curve shall be created.

Percent difference (% D)

$$\%\ D = \frac{Amt_I - Amt_C}{Amt_I} \times 100\ \% \quad (4)$$

where:

Amt_I = amount in standard, and
Amt_C = calculated amount from current CCS.

11.1.3.4 Calibration for Aroclors other than Aroclor 1016 and Aroclor 1260 will be performed by analyzing standards at the concentration representing the midpoint of the calibration range selected. For example, if calibration is desired over the range of 0.02 µg/mL to 0.5 µg/mL, then the 0.1 µg/mL standards shall be used for calibration. Therefore, a five point calibration shall be performed for Aroclors 1016 and 1260 and a one-point calibration shall be performed for all remaining Aroclors.

11.1.3.5 After the linearity of the system has been demonstrated, and each of the remaining Aroclors has been analyzed using middle level concentration, recalibration will be required

only when the calibration check standard criteria is met. Old calibration curves may not be used again, other than to review data generated using those calibration curves.

11.2 *Standardization*:

11.2.1 *Surrogate Recovery*—Recovery control limits for the surrogate are 40 to 150 % recovered.

11.2.1.1 If the recovery is outside of these limits, see Annex A1.

11.2.2 *Method Blank*— For every 20 samples or batch, whichever is more frequent, a method blank shall be prepared by processing the extraction solvent (with surrogate, if used) through the same clean-up as that used for the samples. This is to detect possible contamination picked up during the sample clean-up process.

NOTE 4—A batch is the group of samples prepared at the same time. A batch may not exceed 20 samples.

11.2.3 *Calibration Check Standard (CCS) (Tier II only)*—A 0.1 µg/mL standard (or 0.2 µg/mL) obtained from a source separate from the intermediate standard and containing Aroclors 1016 and 1260 is the CCS which is used to verify the validity of the five-point calibration curve. The calculated results for the CCS shall agree with the current calibration curve to within ±30 % percent difference (% D). If the CCS results indicate that the calibration is outside control limits, and routine maintenance does not correct the problem, then the GC/ECD must be recalibrated.

11.2.4 *Matrix Spike (MS) Samples (Tier II only)*—For every batch or 20 samples, whichever is more frequent, a sample requiring Tier II analysis shall be selected in an unbiased manner and spiked with Aroclor 1268. These results shall be documented, with an example shown in Appendix X2.

11.2.4.1 1.0 mL of 50 µg/mL of Aroclor 1268 (25 µg/mL, if working at lower calibration range) is added to the sample chosen for spiking. Matrix spiked sample recovery limits are from 60 to 140 %, providing any Aroclor present in the sample before spiking does not exceed five times the spike level.

$$\% \text{ Recovery} = \frac{\text{Recovered amount}}{\text{Spiked amount}} \times 100\ \% \quad (5)$$

11.2.5 *Matrix Spike Duplicate (MSD) Sample (Tier II only)*—Every batch or 20 samples, whichever is more frequent, precision data is generated using a matrix spike duplicate. Acceptance criteria is 20 % relative percent difference (RPD) for the duplicate analyses.

11.2.5.1 RPD is calculated from the absolute difference between duplicate percent recovery results D_1 and D_2 divided by the mean value of the duplicates.

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100\ \% \quad (6)$$

12. Procedure

12.1 *Compositing*—It is common to analyze mixtures of multiple samples, called composites, if a large number of samples are analyzed. This approach is described in Annex A3.

12.2 *Sample Preparation Procedure*:

12.2.1 *Liquid Samples*—Accurately pipette 3.0 mL of sample into a tared 40 mL vial (fitted with a TFE-fluorocarbon-lined cap) and weight. *If the results are calculated by weight* accurately weigh the sample and record the weight. Spike this sample with 100 µL of decachlorobiphenyl surrogate working standard.

12.2.1.1 Add 27 mL acetone/hexane to the vial, producing a 1:10 dilution. Cap it and vortex vigorously for at least 30 s. If the sample is not completely miscible with acetone/hexane, add more acetone to reach a total of approximately 30 mL extract and vortex again. (Alternatively, place capped vial in sonic bath for 5 min.)

12.2.2 *Solid, Semi-solids, Sludge Samples*—Weigh accurately 3.0 g of sample into a 40 mL vial fitted with a TFE-fluorocarbon-lined cap. Spike this sample with 100 µL of decachlorobiphenyl surrogate working standard. Add 30 mL of acetone/hexane to the vial for a 1:10 dilution. Vortex for at least 30 s.

12.2.2.1 If the sample does not totally dissolve, vortex again or place capped vial in sonic bath for 5 min. This shall provide adequate contact whether or not any further dissolution occurs.

12.2.3 *Matrix Spike and Matrix Spike Duplicate Samples*—Add 1.0 mL of spiking solution to the sample just after the addition of the surrogate and prior to the addition of the acetone-hexane solvent.

12.2.4 *Centrifuge*—If sediment is visible, centrifuge the extract to separate out the sediment.

12.3 *Sample Clean-up*—Clean-up is not required for all samples; however, interference problems due to the presence of other chemical species may usually be addressed using the procedures found in Annex A4.

12.4 *Gas Chromatographic Analysis Sequence*—Samples are analyzed in a set referred to as an analysis sequence.

12.4.1 *Tier 1–Screening*:

12.4.1.1 *Standards Sequence (initially and optionally with recalibrations)*—(a) Aroclor 1016/1260, at selected IPS level (5 times) and (b) The following may be mixed as described below and shall be analyzed at 0.1 µg/mL each (for 20 mg/Kg level of interest use 0.2 µg/mL).

Aroclor	1221
Aroclor	1232
Aroclor	1242
Aroclor	1248
Aroclor	1254
Aroclor	1262
Aroclor	1268

12.4.1.2 Some of the standards in 12.4.1.1 may be run as mixed standards:

Aroclor	May be Mixed With
1268	1221 or 1232 or 1242 or 1248 or 1254
1262	1221 or 1232 or 1242 or 1248
1254	1221

12.4.1.3 *A Typical Analysis Sequence*—A typical analysis sequence includes (a) reagent blank (optional), (b) Instrument Performance Standard (IPS) (every 20 samples or every day, whichever is more frequent), (c) method blank, and (d) Samples 1 to 20.

12.4.1.4 Repeat this sequence as long as the system meets the IPS criteria.

12.4.2 *Tier 2–Quantitation*:

12.4.2.1 *Standards Sequence*—The standards sequence includes (a) reagent blank, (b) Aroclor 1016/1260 (5 point