

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 136

[EPA-HQ-OW-2014-0797; FRL-9957-24-OW]

RIN 2040-AF48

Clean Water Act Methods Update Rule for the Analysis of Effluent

AGENCY: Environmental Protection Agency (EPA). ACTION: Final rule.

SUMMARY: This rule modifies the testing procedures approved for analysis and sampling under the Clean Water Act. The changes adopted in this final rule fall into the following categories: New and revised EPA methods (including new and/or revised methods published by voluntary consensus standard bodies (VCSB), such as ASTM International and the Standard Methods Committee); updated versions of currently approved methods; methods reviewed under the alternate test procedures (ATP) program; clarifications to the procedures for EPA approval of nationwide and limited use ATPs; and amendments to the procedure for determination of the method detection limit to address laboratory contamination and to better account for intra-laboratory variability. DATES: This regulation is effective on September 27, 2017. The incorporation by reference of certain publications listed in the rule is approved by the Director of the Federal Register as of

September 27, 2017. For judicial review purposes, this final rule is promulgated as of 1:00 p.m. (Eastern time) on September 12, 2017 as provided at 40 CFR 23.2 and 23.7. ADDRESSES: EPA has established a docket for this action under Docket ID No. EPA-HQ-OW-2014-0797. All documents in the docket are listed on the www.regulations.gov Web site. Although listed in the index, some information is not publicly available, e.g., confidential business information (CBI) or other information whose disclosure is restricted by statute. Certain other materials, such as copyrighted material are not placed on the Internet and will be publicly available only in hard copy form. Publicly available docket materials are available either electronically through www.regulations.gov or in hard copy at the Water Docket in EPA Docket Center, EPA/DC, EPA West William J. Clinton Building, Room 3334, 1301 Constitution Ave. NW., Washington, DC. The Public Reading Room is open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The telephone number for the Public Reading Room is 202-566-1744 and the telephone number for the Water Docket is 202-566-2426. FOR FURTHER INFORMATION CONTACT: Adrian Hanley, Engineering and Analysis Division (4303T), Office of Water, Environmental Protection Agency, 1200 Pennsylvania Ave. NW., Washington, DC 20460-0001; telephone:

202-564-1564; email: hanley.adrian@epa.gov. SUPPLEMENTARY INFORMATION: A. General Information 1. Does this Action apply to me? EPA proposed the changes in this method update rule for public comment on February 19, 2015 (80 FR 8956). EPA Regions, as well as States, Territories and Tribes authorized to implement the National Pollutant Discharge Elimination System (NPDES) program, issue permits with conditions designed to ensure compliance with the technology-based and water quality-based requirements of the Clean Water Act (CWA). These permits may include restrictions on the quantity of pollutants that may be discharged as well as pollutant measurement and reporting requirements. If EPA has approved a test procedure for analysis of a specific pollutant, the NPDES permittee must use an approved test procedure (or an approved alternate test procedure if specified by the permitting authority) for the specific pollutant when measuring the required waste constituent. Similarly, if EPA has established sampling requirements, measurements taken under an NPDES permit must comply with these requirements. Therefore, entities with NPDES permits will potentially be affected by the actions in this rulemaking. Entities potentially affected by the requirements of this rule include:

Category	Examples of potentially affected entities
State, Territorial, and Indian Tribal Governments	States, territories, and tribes authorized to administer the National Pollutant Discharge Elimination System (NPDES) permitting program; states, territories, and tribes providing certification under CWA section 401; state, territorial, and tribal owned facilities that must conduct monitoring to comply with NPDES permits.
Industry	Facilities that must conduct monitoring to comply with NPDES permits.
Municipalities	Publicly Owned Treatment Works (POTWs) or other municipality owned facilities that must conduct monitoring to comply with NPDES permits.

This table is not exhaustive, but rather provides a guide for readers regarding entities likely to be affected by this action. This table lists types of entities that EPA is now aware of that could potentially be affected by this action. Other types of entities not listed in the table could also be affected. To determine whether your facility is affected by this action, you should carefully examine the applicability language at 40 CFR 122.1 (NPDES purpose and scope), 40 CFR 136.1 (NPDES permits and CWA) and 40 CFR 403.1 (pretreatment standards purpose and applicability). If you have questions regarding the applicability of this action

to a particular entity, consult the appropriate person listed in the preceding FOR FURTHER INFORMATION CONTACT section. B. What process governs judicial review of this rule? Under Section 509(b)(1) of the Clean Water Act (CWA), judicial review of this CWA rule may be obtained by filing a petition for review in a United States Circuit Court of Appeals within 120 days from the date of promulgation of this rule. For judicial review purposes, this final rule is promulgated as of 1 p.m. (Eastern time) on September 12, 2017 as provided at 40 CFR 23.2.

Section 509(b)(2) provides that any rule (or requirements of any rule) for which review could have been obtained under Section 509(b)(1) may also not be challenged later in civil or criminal proceedings for enforcement. C. Abbreviations and Acronyms Used in the Preamble and Final Rule Text 4AAP: 4-Aminoantipyrine AA: Atomic Absorption ADMI: American Dye Manufacturers Institute AOAC: AOAC International ASTM: ASTM International ATP: Alternate Test Procedure BOD5: 5-day Biochemical Oxygen Demand test CAS: Chemical Abstract Services

CATC: Cyanide Amenable to Chlorination
 CFR: Code of Federal Regulations
 CIE/UV: Capillary Ion Electrophoresis/
 Ultraviolet
 COD: Chemical Oxygen Demand
 CWA: Clean Water Act
 DPD: N,N-diethyl-*p*-phenylenediamine
 DPD-FAS: N,N-diethyl-*p*-phenylenediamine
 with ferrous ammonium sulfate
 EDTA: Ethylenediamine tetraacetic acid
 EPA: Environmental Protection Agency
 FLAA: Flame Atomic Absorption
 Spectroscopy
 GC: Gas Chromatograph/Chromatography
 GC/HSD: Gas chromatography/halogen-
 specific detector
 GC/MS: Gas chromatography/mass
 spectrometry
 HEM: Hexane extractable material
 HPLC: High performance liquid
 chromatography
 HRGC: High Resolution Gas Chromatography
 HRMS: High Resolution Mass Spectrometry
 HSD: Halogen-specific detector
 ICP: Inductively coupled plasma
 ICP/AES: Inductively Coupled Plasma-
 Atomic Emission Spectroscopy
 ICP/MS: Inductively Coupled Plasma-Mass
 Spectrometry
 LCS: Laboratory Control Sample
 MDL: Method Detection Limit
 MS: Mass Spectrometry
 MPN: Most Probable Number
 MS/MSD: Matrix Spike/Matrix Spike
 Duplicate
 NARA: National Archives and Records
 Administration
 NPDES: National Pollutant Discharge
 Elimination System
 NIST: National Institute of Standards and
 Technology
 PAH: Polynuclear aromatic hydrocarbons
 POTW: Publicly Owned Treatment Works
 QA: Quality Assurance
 QC: Quality Control
 RRT: Relative retention time
 SDDC: Silver diethyldithiocarbamate
 SGT-HEM: Silica gel treated-hexane
 extractable material
 SM: Standard Methods
 SPADNS: Common name for fluoride dye
 reagent which is a mixture of chemicals
 STGFAA: Stabilized Temperature Graphite
 Furnace Atomic Absorption Spectroscopy
 TKN: Total Kjeldahl Nitrogen
 TOC: Total Organic Carbon
 USGS: United States Geological Survey
 UV: Ultraviolet
 VCSB: Voluntary Consensus Standards Body
 WET: Whole Effluent Toxicity

Table of Contents

- I. Statutory Authority
- II. Summary of Final Rule
 - A. New Versions of Previously Approved EPA Methods in 40 CFR 136.3 and Appendix A
 - B. Methods Incorporated by Reference
 - C. New Standard Methods and New Versions of Approved Standard Methods in 40 CFR 136.3
 - D. New Versions of Approved ASTM Methods in 40 CFR 136.3
 - E. New United States Geological Survey (USGS) Methods in 40 CFR 136.3
 - F. New ATPs in 40 CFR 136.3

- G. Changes to 40 CFR Part 136 To Align With 40 CFR Part 122
- H. Corrections to 40 CFR Part 136
- I. Changes to Table II at 40 CFR 136.3(e) to Required Containers, Preservation Techniques, and Holding Times
- J. Clarifications/Corrections to ATP Procedures in 40 CFR 136.4, 136.5 and Allowed Modifications in 40 CFR 136.6
- K. Changes to Appendix B to 40 CFR Part 136—Definition and Procedure for the Determination of the Method Detection Limit (MDL)
- III. Changes Between the Proposed Rule and the Final Rule
 - A. Changes to Footnote 30 in Table IA and Footnote 27 in Table IH
 - B. Changes to Table IB
 - C. Changes to Table II
 - D. Change to Method Modifications and Analytical Requirements in § 136.6, Methods Modification Paragraph
 - E. Changes to EPA Method 608.3
 - F. Change to EPA Method 611
 - G. Changes to EPA Method 624.1
 - H. Changes to EPA Method 625.1
 - I. Changes to Method Detection Limit (MDL) Procedure
 - J. Changes to WET Errata
- IV. Statutory and Executive Order Reviews
 - A. Executive Order 12866: Regulatory Planning and Review and Review and Executive Order 13563: Improving Regulation and Regulatory Review
 - B. Paperwork Reduction Act
 - C. Regulatory Flexibility Act
 - D. Unfunded Mandates Reform Act
 - E. Executive Order 13132: Federalism
 - F. Executive Order 13175: Consultation and Coordination With Indian Tribal Governments
 - G. Executive Order 13045: Protection of Children From Environmental Health Risks and Safety Risks
 - H. Executive Order 13211: Actions That Significantly Affect Energy Supply, Distribution, or Use
 - I. National Technology Transfer and Advancement Act of 1995
 - J. Executive Order 12898: Federal Actions to Address Environmental Justice in Minority Populations and Low-Income Populations
 - K. Congressional Review Act

I. Statutory Authority

EPA is promulgating this rule pursuant to the authority of sections 301(a), 304(h), and 501(a) of the Clean Water Act (“CWA”) 33 U.S.C. 1311(a), 1314(h), and 1361(a). Section 301(a) of the CWA prohibits the discharge of any pollutant into navigable waters unless the discharge complies with, among other provisions, a National Pollutant Discharge Elimination System (NPDES) permit issued under section 402 of the CWA. Section 304(h) of the CWA requires the Administrator of the EPA to “* * * promulgate guidelines establishing test procedures for the analysis of pollutants that shall include the factors which must be provided in any certification pursuant to [section

401 of the CWA] or permit application pursuant to [section 402 of the CWA].” Section 501(a) of the CWA authorizes the Administrator to “* * * prescribe such regulations as are necessary to carry out this function under [the CWA].” EPA generally has codified its test procedure regulations (including analysis and sampling requirements) for CWA programs at 40 CFR part 136, though some requirements are codified in other Parts (e.g., 40 CFR chapter I, subchapters N and O).

II. Summary of Final Rule

The following sections describe the changes EPA is making in this final rule. In addition, further information concerning the rule may be found in a document prepared for this rule providing EPA’s responses to comments it received on the proposed rule. That document (“Response to Comments Document for the Methods Update Rule Proposal (80 CFR 8956, February 19, 2015”) is available in the electronic docket listed in the **ADDRESSES** section at the beginning of this document. The following sections describe changes EPA is making in this final rule.

A. New Versions of Previously Approved EPA Methods in 40 CFR 136.3 and Appendix A

This rule approves new versions of already approved EPA methods and corrects typographical errors in the methods. The following briefly describes the EPA methods added to part 136.

1. EPA Methods 608.3, 611, 624.1 and 625.1

Method 608.3, Organochlorine Pesticides and PCBs by GC/HSD. This method measures organochlorine pesticides and polychlorinated biphenyls (PCBs) in industrial discharges and other environmental samples by gas chromatography (GC) combined with a halogen-specific detector (HSD: e.g., electron capture, electrolytic conductivity), as provided under 40 CFR 136.1.

EPA Method 611, Haloethers. This method measures the following haloethers: Bis(2-chloroethyl) ether, bis(2-chloroethoxy) methane, 2, 2’-oxybis (1-chloropropane), 4-bromophenyl phenyl ether, and 4-chlorophenyl phenyl ether in municipal and industrial discharges by gas chromatography (GC) as provided under 40 CFR 136.1. The only change EPA has made is correcting a typographical error in the list of parameters by changing “4-Chlorophenyl phenyl ether” to “4-Chlorophenyl phenyl ether” and has

corrected an analyte name to 2,2'-oxybis(1-chloropropane), which matches the CAS Number 108-60-1.

EPA Method 624.1, Purgeables by GC/MS. This method measures purgeable organic pollutants in industrial discharges and other environmental samples by gas chromatography (GC) combined with mass spectrometry (MS), as provided under 40 CFR 136.1.

EPA Method 625.1, Base/Neutrals and Acids by GC/MS. This method measures semivolatile organic pollutants in industrial discharges and other environmental samples by GC/MS, as provided under 40 CFR 136.1.

2. EPA Methods 1600, 1603, 1680, and 1682

This rule implements the following changes for EPA microbiological methods 1600, 1603, 1680, and 1682 that correct typographical or other errors that EPA identified in the methods after publication. This rule revises all of these methods with new EPA document numbers and dates.

EPA Method 1600 for Enterococci using membrane filtration: In Table 3 Verification controls, EPA changed the negative control for brain heart infusion broth incubated at 45 °C from *Escherichia coli* to *Enterobacter aerogenes*. *E. coli* is thermotolerant and *E. aerogenes* is not, so *E. coli* is not an appropriate negative control when heated.

EPA Method 1603 for *E. coli* using membrane filtration: In section 11.5, EPA changed the number of colonies on a countable plate from 20–60 to 20–80 colonies. Sixty colonies was a typographical error. In addition, the following sentence was inadvertently omitted and EPA included it: Sample volumes of 1–100 mL are normally tested at half-log intervals (e.g., 100, 30, 10, and 3 mL).

EPA Method 1680 for fecal coliforms using multiple tube fermentation: In section 3.1 Definitions, the sentence “The predominant fecal coliform is *E. coli*.” now reads “The predominant fecal coliform can be *E. coli*.”

EPA Method 1682 for *Salmonella* by MSRV medium: (1) In section 9.3, Table 2, the lab-prepared spike acceptance criteria now reads: “Detect–254%” and “Detect–287%” and (2) in section 14.5, Table 9, the spiked *Salmonella* for Example 2, Liquid now reads “ 3.7×10^8 CFU/mL.”

B. Methods Incorporated by Reference

Currently, hundreds of methods and ATPs are incorporated by reference within 40 CFR part 136. In most cases, 40 CFR part 136 contains multiple approved methods for a single pollutant

and regulated entities often have a choice in the selected method. This rule incorporates by reference revisions to methods from two VCSBs: Standard Methods and ASTM. The VCSB methods in this rule are in compliance, as discussed more fully in Section IV.I below, with the National Technology Transfer Act which directs EPA to use voluntary consensus standards so long as they are consistent with applicable law and not otherwise impractical. The methods are available on their respective VCSB Web sites to everyone at a cost determined by the VCSB, generally from \$40 to \$80. Both organizations also offer memberships or subscriptions that allow unlimited access to their methods. The cost of obtaining these methods is not a significant financial burden for a discharger or environmental laboratory, making the methods reasonably available. This rule also includes USGS methods and vendor ATPs that are incorporated by reference. The ATPs and USGS methods are available free of charge on the Web site for that organization. Therefore, EPA concludes that the methods and Alternate Test Procedures (ATPs) incorporated by reference are reasonably available. The individual standards are discussed in greater detail below.

C. New Standard Methods and New Versions of Approved Standard Methods in 40 CFR 136.3

This rule approves new versions of currently approved Standard Methods. The new versions of currently approved Standard Methods clarify or improve the instructions in the method, improve the QC requirements, or make editorial corrections. Consistent with the previous method update rule (77 FR 29758, May 18, 2012), EPA generally approves and includes in 40 CFR part 136 only the most recent version of a method published by the Standard Methods Committee by listing only one version of the method with the year of publication designated by the last four digits in the method number (e.g., SM 3111 B–2011). The date indicates the latest revision date of the method. This allows use of a specific method in any edition that includes a method with the same method number and year of publication.

Most of the revisions included to Standard Methods in this rule do not contain any substantive changes. Each Standard Method entry contains the Standard Methods number and date, the parameter, and a brief description of the analytical technique. The methods listed below are organized according to

the table at 40 CFR part 136 in which they appear.

The following identifies new versions of previously approved Standard Methods that EPA is including in Table IB at 40 CFR part 136. Where there are substantive changes to the method, these are noted:

1. SM 2120 B–2011, color, platinum cobalt visual comparison method.

2. SM 2120 F–2011, color, ADMI weighted-ordinate spectrophotometer method. EPA previously approved this method as SM 2120 E–1993. It is also similar to the currently approved National Council for Air and Stream Improvement, Inc. method that uses American Dye Manufacturers Institute weighted-ordinate spectrophotometric parameters. A footnote on the method specifies that the pH should be 7.6 and not 7.0 when used for NPDES monitoring purposes, since the original method was approved with a reference pH of 7.6. Additionally, the currently approved methods for the Color parameter are assigned more specific parameter names.

3. SM 2130 B–2011, turbidity, nephelometric method.

4. SM 2310 B–2011, acidity, titration using electrometric endpoint or phenolphthalein endpoint.

5. SM 2320 B–2011, alkalinity, electrometric or colorimetric titration to pH 4.5.

6. SM 2340 B–2011 and SM 2340 C–2011, hardness, by the calculation method or EDTA titration.

7. SM 2510 B–2011, conductivity, Wheatstone bridge method.

8. SM 2540 B–2011, SM 2540 C–2011, SM 2540 D–2011, SM 2540 E–2011, and SM 2540 F–2011, total, filterable, non-filterable, volatile, and settleable residue (solids, listed in the same order as the method numbers), all by gravimetric methodologies.

9. SM 2550 B–2010, temperature, thermometric.

10. SM 3111 B–2011, SM 3111 C–2011, SM 3111 D–2011, and SM 3111 E–2011, metals, direct aspiration atomic absorption (AA) methods with different gas mixtures. Each method has a different list of metals; these lists were not changed.

11. SM 3112 B–2011, metals, applicable to mercury, cold-vapor atomic absorption spectrometric method.

12. SM 3113 B–2010, metals, electrothermic atomic absorption spectrometric method. The only substantive change is a reduction in the required replicate analyses of each calibration standard from three to two. Similar EPA methods do not require replicates of each calibration standard.

13. SM 3114 B–2011 and SM 3114 C–2011, total arsenic and total selenium, hydride generation/atomic absorption spectrometric methods. Both analyze total arsenic and total selenium.

14. SM 3120 B–2011, metals, inductively coupled plasma (ICP) method; no changes were made to the approved list of metals.

15. SM 3125 B–2011, metals, inductively coupled plasma/mass spectrometry (ICP/MS) method; no changes were made to the approved list of metals.

16. SM 3500-Al B–2011, aluminum, colorimetric method.

17. SM 3500-As B–2011, arsenic, colorimetric method silver diethyldithiocarbamate (SDDC) method.

18. SM 3500-Ca B–2011, calcium, titrimetric method (EDTA).

19. SM 3500-Cr B–2011 and SM 3500-Cr C–2011, chromium. The “B” method uses a colorimetric method (diphenylcarbazide) and is approved for total or dissolved chromium. The “C” method uses ion chromatography and is only approved for dissolved chromium.

20. SM 3500-Cu B–2011 and SM 3500-Cu C–2011, copper. Both method sections use colorimetric methods. The “B” method uses a neocuproine reagent, and the “C” method uses a bathocuproine reagent.

21. SM 3500-Fe B–2011, iron, colorimetric method (phenanthroline).

22. SM 3500-K B–2011 and SM 3500-K C–2011, potassium. The “B” method is a flame photometric method, and the “C” method is an electrode method.

23. SM 3500-Mn B–2011, manganese, colorimetric method (persulfate).

24. SM 3500-Na B–2011, sodium, flame photometric method.

25. SM 3500-Pb B–2011, lead, colorimetric method (dithizone).

26. SM 3500-V B–2011, vanadium, colorimetric method (gallic acid).

27. SM 3500-Zn B–2011, zinc, colorimetric method (zincin).

28. SM 4110 (B–D)–2011, anions, ion chromatography; no changes were made to the approved analyte list.

29. SM 4140 B–2011, inorganic anions, capillary ion electrophoresis with indirect ultraviolet (UV) detection: No changes were made to the approved analyte list.

30. SM 4500-B B–2011, boron, spectrophotometer or filter photometer (curcumin)

31. SM 4500-Cl[−] (B–E)–2011, chloride, titrimetric: (Silver nitrate), (mercuric nitrate), automated (ferricyanide), potentiometric titration.

32. SM 4500-Cl (B–G)–2011, chlorine (residual), amperometric direct, amperometric direct (low level), iodometric direct, back titration ether

end–point, titrimetric: N,N-diethyl-*p*-phenylenediamine with ferrous ammonium sulfate (DPD-FAS), spectrophotometric (DPD).

33. SM 4500-CN[−] (B–G)–2011, cyanide, manual distillation with MgCl₂ followed by: Titrimetric, spectrophotometric, manual, ion selective electrode, cyanide amenable to chlorination (CATC); manual distillation with MgCl₂, followed by: Titrimetric or spectrophotometric.

34. SM 4500-F[−] (B–E)–2011, fluoride, manual distillation, followed by any of the following: Electrode, manual, colorimetric, fluoride dye reagent (SPADNS is the common name for the fluoride dye reagent which is a mixture of chemicals), automated complexone.

35. SM 4500-H⁺ B–2011, hydrogen ion (pH), electrometric measurement.

36. SM 4500-NH₃ (B–H)–2011, ammonia (as nitrogen), manual distillation or gas diffusion (pH > 11), followed by any of the following: Titration, electrode, manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods;

automated phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.

37. SM 4500-NO₂[−] B–2011, nitrite (as nitrogen), spectrophotometric: Manual.

38. SM 4500-NO₃[−] D–2011, nitrate (as nitrogen), ion selective electrode.

39. SM 4500-NO₃[−] (E, F, H)–2011, nitrate-nitrite (as nitrogen), colorimetric: Cadmium reduction-manual and automated, and colorimetric: Automated hydrazine.

40. SM 4500-NO₃[−] (E, F)–2011, nitrite (as nitrogen), colorimetric: Cadmium reduction-manual and automated.

41. SM 4500-N_{org} (B–D)–2011, total Kjeldahl nitrogen (as nitrogen, organic), semi-automated block digester colorimetric (distillation not required).

42. SM 4500-O (B–G)–2011, oxygen (dissolved), Winkler (azide modification), electrode.

43. SM 4500-P (B(5), E–H)–2011, phosphorus and ortho-phosphate, persulfate digestion, digestion, followed by any of the following: Manual or automated ascorbic acid reduction. The “B Part 5” method is the persulfate digestion procedure and is required prior to measurement of total phosphorus using SM 4500 P (E–H). The “E” through “G” methods are approved for both total phosphorus and ortho-phosphate. The “H” method is only approved for total phosphorous.

44. SM 4500-S^{2−} (B–D, F, G)–2011, sulfide, sample pretreatment, titrimetric (iodine) analysis, colorimetric (methylene blue), ion selective electrode.

45. SM 4500-SiO₂ (C, E, F)–2011, silica, 0.45-micron filtration followed by any of the following: Colorimetric, manual or automated (molybdosilicate).

46. SM 4500-SO₃^{2−} B–2011, sulfite, titrimetric (iodine-iodate).

47. SM 4500-SO₄^{2−} (C–G)–2011, sulfate, automated colorimetric, gravimetric, and turbidimetric.

48. SM 5210 B–2011, biochemical oxygen demand (BOD₅), dissolved oxygen depletion.

49. SM 5220 (B–D)–2011, chemical oxygen demand (COD), titrimetric; spectrophotometric, manual or automatic.

50. SM 5310 (B–D)–2011, total organic carbon (TOC), combustion, heated persulfate or UV persulfate oxidation.

51. SM 5520 (B, F)–2011, oil and grease, hexane extractable material (HEM): *n*-hexane extraction and gravimetry, silica gel treated HEM (SGT–HEM): Silica gel treatment and gravimetry.

52. SM 5530 (B, D)–2010, phenols, manual distillation, followed by colorimetric 4-aminoantipyrine (4AAP) manual.

53. SM 5540 C–2011, surfactants, colorimetric (methylene blue).

The following identifies new versions of previously approved Standard Methods that EPA is including in Table IC at 40 CFR part 136:

1. SM 6200 (B, C)–2011, volatile organic compounds, purge and trap capillary-column gas chromatographic/mass spectrometric (GC/MS), purge and trap capillary-column gas chromatographic (GC)

2. SM 6440 B–2005, polynuclear aromatic hydrocarbons (PAHs), high performance liquid chromatography (HPLC)

The following identifies new versions of previously approved methods that EPA is including in Table ID at 40 CFR part 136:

1. SM 6630 (B, C)–2007, organochlorine pesticides, gas chromatography (GC)

2. SM 6640 B–2006, acidic herbicide compounds, gas chromatography (GC)

EPA also revised the approval of certain Standard Methods previously approved in part 136 for which Standard Methods adopted updates that contain substantive changes. The following summarizes these changes for each method, organized by the table at 40 CFR part 136 in which they appear.

The following identifies previously approved Standard Methods in Table IA and/or Table IH at 40 CFR part 136 Table IB at 40 CFR part 136 where there are substantive changes to the method:

1. EPA replaced the membrane filtration method SM 9222 B–1997 with

SM 9222 B–2006. This method analyzes Coliform (total) in the presence of chlorine. The newer method includes a number of technology updates that do not significantly change the procedure. In addition, the method:

a. Modified the procedure to allow for the use of a humidified incubator if loose-lidded plates are used during incubation.

b. Added a note that five typical and five atypical colonies per membrane need to be identified during coliform verification.

c. Moved the definition of “Coliform” that was Section 4 of SM 9222, and renumbered the rest of the document, such that the “Procedure” is now Section 4, instead of Section 5. This is not a substantive change except that in Table IA, Parameter 4 “Coliform (total), in presence of chlorine, number per 100 mL” the citation for “MF with enrichment” will be changed from “9222 (B+B.5c)–1997” to “9222 (B+B.4c)–2006.”

2. This rule replaces the membrane filtration method SM 9222 D–1997 with SM 9222 D–2006. This method analyzes Coliform (fecal) and Coliform (fecal) in the presence of chlorine. The new method allows use of a dry recirculating incubator as specified in the culture dishes section. In addition, this rule adds the following footnote to Tables IA and IH regarding SM 9222 D–2006 for fecal coliform verification frequency: “The verification frequency is at least five typical and five atypical colonies per sampling site on the day of sample collection & analysis.” SM 9222 D–2006 specifies that the fecal coliform colonies should be verified “at a frequency established by the laboratory,” which can be as low as zero. Colonies need to be verified to prevent misidentification of results as false positive or false negative.

3. This rule replaces the membrane filtration method SM 9222 G–1997 with SM 9222 G–2006 in Table IH. These methods analyze for *E. coli* and Fecal Coliforms. The newer method includes a number of technology updates that do not significantly change the procedure. In addition, the method now has a modified composition of EC broth to include different quantities of KH_2PO_4 and 4-methylumbelliferyl- β -D-glucuronide.

D. New Versions of Approved ASTM Methods in 40 CFR 136.3

This rule approves new versions of currently approved ASTM methods, for the same reasons outlined in the first paragraph of Section II.B above. Many of the new versions of ASTM Methods approved in 40 CFR part 136 do not

contain any substantive changes. Each entry contains (in the following order): Approved ASTM method number and date, the parameter, a brief description of the analytical technique. Where there were substantive changes, they are identified. The methods listed below are organized according to the table at 40 CFR part 136 in which they appear.

The following identifies new versions of currently approved ASTM methods that are included in Table IB at 40 CFR part 136:

1. ASTM D 511–09 (A, B), calcium and magnesium, titrimetric ethylenediamine tetraacetic acid (EDTA), AA direct aspiration.
2. ASTM D 516–11, sulfate ion, turbidimetric.
3. ASTM D 858–12 (A–C), manganese, atomic absorption (AA) direct aspiration, AA furnace.
4. ASTM D 859–10, silica, colorimetric, manual.
5. ASTM D 1067–11, acidity or alkalinity, electrometric endpoint or phenolphthalein endpoint; electrometric or colorimetric titration to pH 4.5, manual.
6. ASTM D 1068–10 (A–C), iron, AA direct aspiration; AA furnace; colorimetric (phenanthroline).
7. ASTM D 1126–12, hardness, titrimetric (EDTA).
8. ASTM D 1179–10 (A, B), fluoride ion, electrode, manual; colorimetric, (SPADNS).
9. ASTM D 1246–10, bromide ion, electrode.
10. ASTM D 1687–12 (A–C), chromium (total) and dissolved hexavalent chromium, colorimetric (diphenyl-carbazide); AA direct aspiration; AA furnace.
11. ASTM D 1688–12 (A–C), copper, AA direct aspiration, AA furnace.
12. ASTM D 1691–12 (A, B), zinc, AA direct aspiration.
13. ASTM D 1976–12, dissolved, total-recoverable, or total elements, inductively coupled plasma/atomic emission spectroscopy (ICP/AES).
14. ASTM D 3223–12, total mercury, cold vapor, manual.
15. ASTM D 3373–12, vanadium, AA furnace.
16. ASTM D 3557–12 (A–D), cadmium, AA direct aspiration, AA furnace, voltammetry.
17. ASTM D 3590–11 (A, B), total Kjeldahl nitrogen, manual digestion and distillation or gas diffusion; semi-automated block digester colorimetric (distillation not required).
18. ASTM D 4382–12, barium, AA furnace.
19. ASTM D 4658–09, sulfide ion, ion selective electrode.

20. ASTM D 5257–11, dissolved hexavalent chromium, ion chromatography.

21. ASTM D 5673–10, dissolved elements and total-recoverable elements, ICP/MS.

22. ASTM D 5907–13, filterable matter (total dissolved solids) and nonfilterable matter (total suspended solids), gravimetric, 180 °C gravimetric, 103–105 °C post washing of residue.

23. ASTM D 6508–10, inorganic anions (fluoride, bromide, chloride, nitrite, nitrate, orthophosphate, and sulfate), capillary ion electrophoresis with indirect UV detection.

24. ASTM D 7284–13, total cyanide, manual distillation with MgCl_2 followed by flow injection, gas diffusion amperometry.

25. ASTM D 7511–12, total cyanide, segmented flow injection, in-line ultraviolet digestion, followed by gas diffusion amperometry.

EPA has changed Table IC at 40 CFR part 136 as follows:

1. ASTM D 7065–11, nonylphenol, bisphenol A, *p*-tert-octylphenol, nonylphenol monoethoxylate, nonylphenol diethoxylate, gas chromatography/mass spectrometry (GC/MS).

E. New United States Geological Survey (USGS) Methods in 40 CFR 136.3

1. This rule adds USGS Methods I–2547–11 and I–2548–11 titled “Colorimetric Determination of Nitrate Plus Nitrite in Water by Enzymatic Reduction, Automated Discrete Analyzer Methods,” to Table IB for the analytes nitrate, nitrite, and combined nitrate-nitrite. Method I–2548–11 is a low level (analytical range) version of Method I–2547–11. Both methods are included in the same method title. The method can be found in USGS Survey Techniques and Methods, Book 5, Chapter B8. The method is available at no cost from the USGS Web site. This method follows the same procedure as in ATP Case No. N07–0003—Nitrate Elimination Company Inc.’s (NECi) Method N07–0003, Revision 9.0, March 2014, “Method for Nitrate Reductase Nitrate-Nitrogen Analysis,” which EPA approved in this rule.

F. New ATPs in 40 CFR 136.3

This rule approves six methods submitted to EPA for review through the alternate test procedures (ATP) program and deemed acceptable based on the evaluation of documented method performance.

The following ATP has nationwide approval for wastewater and is incorporated into Table IA:

1. IDEXX Laboratories, Inc., Colilert®-18, “Coliform/ Test for Fecal Coliforms in Wastewater” (ATP Case No. N09-0004). The method is similar to the already approved *E. coli* Colilert®-18 method, with the addition of an increased incubation temperature for fecal coliforms, which requires the use of a waterbath incubator. The Colilert®-18 Coliform/ Substrate Test can be obtained from IDEXX Laboratories Inc., One IDEXX Drive, Westbrook, ME 04092. Telephone: 800-321-0207.

The following four ATPs have nationwide approval for all matrix types and are incorporated into Table IB:

1. The Nitrate Elimination Company Inc. (NECi) Method N07-0003, “Nitrate Reductase Nitrate-Nitrogen Analysis,” Revision 9.0, dated March 2014 (The Nitrate Elimination Company, Inc., 2014a). The analysis measures nitrate, nitrite, and combined nitrate-nitrite. NECi Method N07-0003 is a “green” alternative to the other approved methods which use cadmium, a known carcinogen for the reduction of nitrate to nitrite prior to analyses. NECi Method N07-0003 can be obtained from The Nitrate Elimination Company, 334 Hecla Street, Lake Linden, Michigan, 49945. Telephone: 888-NITRATE.

2. Timberline Instruments, LLC Method Ammonia-001, “Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Conductivity Cell Analysis,” dated June 24, 2011 (Timberline Instruments, LLC 2011a). Timberline Instruments, LLC Method Ammonia-001 can be obtained from Timberline Instruments, LLC, 1880 South Flatiron Court, Boulder, Colorado 80301. Telephone: 303-440-8779.

3. Hach Company Method 10242, “Simplified Spectrophotometric Measurement of Total Kjeldahl Nitrogen in Water and Wastewater,” Revision 1.1, dated January 10, 2013 (Hach Company 2013a). Hach Company Method 10242 is a simplified green chemistry alternative to the other approved methods for measuring TKN. The method uses less toxic reagents (e.g., eliminating the use of mercuric sulfate). Hach Company Method 10242 can be obtained from Hach Company, 5600 Lindbergh Drive, Loveland, CO 80539. Telephone: 970-669-3050.

4. Hach Company Method 10206, “Spectrophotometric Measurement of Nitrate in Water and Wastewater,” Revision 2.1, dated January 10, 2013 (Hach Company 2013b). Hach Company Method 10206 is a “green” alternative to the other approved methods which use cadmium, a known carcinogen for the reduction of nitrate to nitrite prior to analyses. Hach Company Method 10206

can be obtained from Hach Company, 5600 Lindbergh Drive, Loveland, CO 80539. Telephone: 970-669-3050.

The following ATP has nationwide approval for only pulp, paper and paperboard mill biologically treated effluent and is incorporated into Table IB:

1. National Council for Air and Stream Improvement, Inc. (NCASI) Method TNTP-W10900, “Total (Kjeldahl) Nitrogen (TKN) and Total Phosphorus in Pulp and Paper Biologically Treated Effluent by Alkaline Persulfate Digestion,” dated June 2011 (National Council for Air and Stream Improvement, Inc. 2011a). NCASI Method TNTP-W10900 can be obtained from The National Council for Air and Stream Improvement, Inc., Publications Coordinator, P.O. Box 13318, Research Triangle Park, NC 27709-3318, Telephone: 919-941-6400.

G. Changes to 40 CFR Part 136 To Align With 40 CFR Part 122

This rule amends 40 CFR 136.1 to substitute the term “Director” for the terms “Administrator” and “State having an authorized program.” In addition, the rule amends 40 CFR 136.2(d) to state that the term “Director” by cross-reference to the definition of “Director” in the NPDES regulations at 40 CFR 122.2.

EPA eliminated the words “be sufficiently sensitive and” from 40 CFR 136.6(b)(2) to eliminate unnecessary confusion with the term “sufficiently sensitive,” as used in 40 CFR 122. Deleting this term did not change the requirements of 40 CFR 136.6(b)(2).

H. Corrections to 40 CFR Part 136

This rule corrected typographical errors, updated methods from VCSBs that went unnoticed during the last update to 40 CFR part 136, and added technology updates to toxicity methods.

1. This rule makes multiple clarifications and corrections to the Whole Effluent Toxicity acute and chronic methods manuals (Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, EPA-821-R-02-012, October 2002; Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, EPA/821-R-02/013, October 2002; and Methods for Measuring the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, EPA/821-R-02/014, October 2002) listed in Table IA. Clarifications included definition of terms (e.g., the acronym YCT—yeast, cereal leaves, and trout chow, was not

defined), consistency corrections among the three manuals, notation that Cusum figure axes should be log scale, pH and temperature measurements should be done at the beginning of the test (rather than only at the end of the test), etc. Corrections also included deletion of unavailable products, typographical errors, etc. Among the corrections that EPA proposed was a change to the language for Fathead Minnows, Daphnids, and Green Alga in the document *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms*, Fourth Edition, U.S. Environmental Protection Agency, Office of Water, Washington, DC EPA/821-R-02/013, October 2002. For Fathead Minnows and Daphnids, EPA proposed to change “Conductivity, alkalinity, and hardness are measured in each new sample (100% effluent or receiving water) and in the control” to read “Conductivity, alkalinity, and hardness are measured at the beginning of the test for all test concentrations in each new sample and in the control before they are dispersed to the test chambers.” EPA received a number of comments stating that this change would constitute a change to the test rather than a correction or clarification. EPA is in agreement with these comments, and for that reason, will not add the inserted language “at the beginning of the test for all test concentrations.” EPA is retaining its deletion of “(100% effluent or receiving water)” and the insertion of “before they are dispensed to the test chamber” to the end of the sentence. Thus, the sentence will now read “Conductivity, alkalinity, and hardness are measured in each new sample and in the control before they are dispensed to the test chamber.” For Green Alga, the proposed change has been eliminated from the errata because only the increased testing was proposed.

2. This rule changes the Standard Method listed for *E. coli* most probable number (MPN) in Tables IA and IH. During a previous revision, Standard Methods added sampling as section 9221 B.1. As a result, section 9221 B.1 in previously approved versions has become section 9221 B.2. EPA changed SM 9221 B.1 to 9221 B.2 in Tables IA and IH for *E. coli* MPN. The related footnotes in Tables IA and IH (12, 14 and 11, 13, respectively) are accurate and EPA did not propose to change them.

3. This rule adds a line for Enterococci that was erroneously deleted in the 2012 Methods Update Rule. The line states “MPN, multiple

tube” with Standard Method 9230B–2007.

4. This rule revises a hardness entry in Table IB to state “Ca plus Mg as their carbonates, by any approved method for Ca and Mg (See Parameters 13 and 33), provided that the sum of the lowest point of quantitation for Ca and Mg is below the NPDES permit requirement for Hardness.” Previously, this was only allowed for inductively coupled plasma or AA direct aspiration Ca and Mg methods. The rationale behind this change is that if one calcium and magnesium method approved by EPA can be used to calculate hardness, then other EPA approved methods should also be permitted to do so.

5. This rule deletes “p 14” from footnote 24 of Table IB because the method is not on that page.

6. This rule deletes Method 200.5, in Table IB from the cobalt, molybdenum and thallium entries. These analytes have not undergone formal testing by this method, and this method should not have been approved for these analytes.

7. This rule removes the reference to costs in 40 CFR 136.3(b) because costs are not included in the referenced documents.

8. This rule removes the first instance of “are” in 40 CFR 136.3(e) because it is a typographical error.

I. Changes to Table II at 40 CFR 136.3(e) to Required Containers, Preservation Techniques, and Holding Times

This rule revises Table II at 40 CFR 136.3(e) as follows.

1. The rule adds rows to Table II that specify holding times for total/fecal coliforms, and fecal streptococci in Table IH. Previously the holding times for these bacterial tests were unspecified. Now these methods have the same holding time requirements as the other bacterial tests.

2. This rule changes the sodium thiosulfate concentrations in Table II for bacterial tests from 0.0008% sodium thiosulfate to 0.008%. EPA proposed this change in its last update to 40 CFR part 136 (75 FR 58066–58067), but inadvertently omitted it in the publication of the final rule.

3. The rule re-inserts language that was accidentally deleted from footnote 5 of Table II during the previous update to 40 CFR part 136. Footnote 5 now reads “ASTM D7365–09a specifies treatment options for samples containing oxidants (e.g., chlorine) for cyanide analysis. Also, Section 9060A of Standard Methods for the Examination of Water and Wastewater (20th and 21st editions) addresses dechlorination procedures for

microbiological analyses.” Previously, the words: “for microbiological analyses,” were not present, so the footnote did not specify that treatment options for samples containing oxidants is specifically for cyanide analysis, and that the dechlorination procedures are specifically for microbiological analyses.

4. EPA requested public comment on how to approve variances to sample preservation, containers or holding times listed in Table II for specific dischargers. Currently, 40 CFR 136.3(e) grants authority to either the permitting authority in the Region or the Regional ATP Program Coordinator to grant exceptions to Table II for a specific discharger.

Of the eight comments received, four commenters thought that the permitting authority should have the sole authority to approve these variance requests. Three commenters thought that the Regional ATP Program Coordinators should have sole authority to approve variance requests, and one commenter thought that the best approach was for the permitting authority and the Regional ATP Program Coordinator to approve Table II variances for specific dischargers collaboratively. Each of these commenters provided sound reasoning for their suggested approach to the review and approval of these types of requests.

EPA has chosen to defer any decision on revising the current language and to leave 40 CFR 136.3(e) unchanged in this final rule.

J. Clarifications/Corrections to ATP Procedures in 40 CFR 136.4, 136.5 and Allowed Modifications in 136.6

40 CFR 136.4 and 136.5 describe EPA procedures for obtaining approval to use an alternate test procedure either on a national basis, or for limited use by dischargers or facilities specified in the approval. In the 2012 Method Update Rule, EPA made several clarifying changes to the language of these sections. At the same time, however, in many places in 40 CFR 136.4 and 136.5 where the phrase “Regional Alternate Test Procedures Coordinator” or “Regional ATP Coordinator” appears, EPA inadvertently also inserted the phrase “or permitting authority” following the phrase. This error resulted from the use of the “search and replace” function on the computer. The effect of the change was to inadvertently authorize State permitting authorities to approve ATPs for limited use within the State. EPA never intended this result, as is demonstrated by two facts. First, in its proposal for the 2012 Update (75 FR 58024, September 23, 2010), EPA did

not propose to authorize State NPDES permitting authorities to approve limited use ATPs. Second, the rule states that the approval may be restricted to specific dischargers or facilities, or to all dischargers or facilities “specified in the approval for the Region.” (emphasis added). This language evidenced EPA’s intent that only the Region—not the State—would be authorized to issue any such limited use ATP approval. Finally, as further evidence of EPA’s intent, in several places, the text of the rule only makes sense if read to authorize only the Regional ATP Coordinator, not the State permitting authority, to approve limited use ATPs. For example, 40 CFR 136.5(d)(1) provides that after a review of the application by the Alternate Test Procedure Regional ATP Coordinator or permitting authority, the Regional ATP Coordinator or permitting authority notifies the applicant and the appropriate State agency of approval or rejection of the use of the alternate test procedure. As previously written, if the State is acting on a request for approval, the regulation would require the State to inform itself of its own action in approving or rejecting the ATP, a superfluous requirement.

This rule deletes all instances of “or permitting authority” from 40 CFR 136.4 and 136.5 to correct this error and revise the rule text to its original intent. Based on this revision, EPA and EPA alone has the authority to approve limited use ATPs.

This rule also changes 40 CFR 136.4 and 136.5 to clarify the process for nationwide ATP approvals and the Regional ATP Coordinator’s role in limited use ATP approvals. These changes do not significantly change the process; the intent is to make the text simpler and clearer.

Finally, this rule adds language to 40 CFR 136.6(b)(1) to clarify that if a method user is uncertain whether or not a modification is allowed under 40 CFR 136.6, the user should contact either their Director or EPA Regional ATP Coordinator.

K. Changes to Appendix B to 40 CFR Part 136—Definition and Procedure for the Determination of the Method Detection Limit (MDL)

EPA is revising the procedure for determination of the MDL primarily to address laboratory blank contamination and to better account for intra-laboratory variability. The MDL procedure has not been revised since it was originally promulgated in 1983. The suggestion for these revisions came first from The National Environmental Laboratory Accreditation Conference (NELAC)

Institute. EPA proposed to adopt these revisions. Following proposal, EPA further evaluated the proposed revision in conjunction with input from the states and commercial laboratories. EPA received extensive comments on the proposed revisions.

The revisions address the following issues and add new requirements in the following areas.

Background contamination. Under the revisions to appendix B, laboratories are required to evaluate the MDL to account for background levels of contamination. As laboratory methods become more and more sensitive, background levels of contamination are more likely to contribute to the result. These revisions will reduce false positive detects.

MDLs that represent multiple instruments. Under the revisions, if a laboratory uses MDL values that represent multiple instruments, then the laboratory is required to calculate the MDL by analyzing MDL samples and method blanks on all of these instruments. (*Note:* MDL samples are a reference matrix, such as reagent water, spiked with a known and consistent quantity of the analyte.) Previously, laboratories were known to run all of their prepared MDL samples on the most sensitive instrument, and then use that MDL for other instruments. This modification makes the MDL more representative of the laboratory's actual analytical capability. Deriving an MDL that is representative of multiple instruments is an option, not a requirement; laboratories can determine individual MDL values for individual instruments if they prefer.

Under the revisions, laboratories are required to run MDL samples and method blanks every quarter that samples are analyzed using a specific method. Previously, laboratories redetermined the MDL once a year, often under the most ideal circumstances (e.g., immediately after the instrument has been serviced or after an annual maintenance routine). Quarterly MDL samples and method blanks will determine if the detection limit has significantly drifted over time. Laboratories will be exempt from running the quarterly MDL samples and method blanks for a method during quarters when no samples are analyzed using that method. The ongoing quarterly MDL samples and method blanks are used to calculate the MDL every year, recalculation of the MDL is required once every thirteen months. Thirteen months was selected to give laboratories more flexibility. For example, a laboratory can recalculate an MDL on January 8th one year and then

January 17th the next, and still be in compliance.

EPA received comments from industries that purchase laboratory services that stated the revised MDL procedure may increase laboratory costs, but not significantly. EPA also received comments from some laboratories stating the revised MDL procedure would impose increased costs to laboratories, while other laboratories stated the opposite. The majority of commenters supported the revised MDL procedure. All of the laboratory associations, who represent the laboratory community, commented in favor of the revised MDL procedure. Comments not in favor of the MDL revision were received from individual laboratories, individuals, one utility, and two state government departments.

As a result of the comments, EPA has made minor clarifications to the MDL procedure. Two options were added to the MDL procedure as a result of comments received: (1) A streamlined approach to determine whether a new instrument can be added to a group of instruments with an already established MDL and (2) laboratories have the option to use only the last six months of method blank data or the fifty most recent method blanks, whichever yields the greater number of method blanks to calculate the MDL value derived from method blanks (MDLb). Both of these changes are in line with the goals of the revised MDL procedure, and are responsive to the comments received. Neither of these additions are mandatory; however, they provide the laboratory with more options for calculating the MDL. Commenters also noted that the detection limit definition in § 136.2(f) should undergo a minor revision to match the revisions in the MDL procedure (which the definition references). The words, "distinguishable from the method blank results" has been replaced with "greater than zero" in the definition.

III. Changes Between the Proposed Rule and the Final Rule

Except as noted below, the content of the final rule is the same as that of the proposed rule.

A. Changes to Footnote 30 in Table IA and Footnote 27 in Table IH

These footnotes regard SM 9222 D–2006 for fecal coliform verification frequency. EPA proposed a requirement of "at least five typical and five atypical colonies per sampling site on the day of collection and analysis." A number of commenters identified deficiencies with the proposed changes. After further review, EPA has determined that

footnote 30 in Table IA and footnote 27 in Table IH require both modification and clarification and is changing both footnotes to read "On a monthly basis, at least ten blue colonies from the medium must be verified using Lauryl Tryptose Broth and EC broth, followed by count adjustment based on these results; and representative non-blue colonies should be verified using Lauryl Tryptose Broth. Where possible, verifications should be done from randomized sample sources."

B. Changes to Table IB

As pointed out by multiple commenters, and verified by EPA, the color parameter in Table IB contains methodologies and methods that are mislabeled. EPA reorganized the Color methodology descriptions and methods as follows: (1) The ADMI colorimetric procedure SM 2120 F–2011 is now listed on a new "ADMI" methodology row. (2) Footnote 18 is listed on the table row with the methodology "spectrophotometric," and footnote 18 lists both NCASI Technical Bulletin 253 (1971) and NCASI Technical Bulletin 803 (2000). NCASI Technical Bulletin 803 is an update to NCASI Technical Bulletin 253 for the measurement of color in pulp mill wastewaters. The update adds a stabilizing pH buffer and turbidity reduction approaches. (3) SM 2120 B–2011 and USGS Method I–1250–85 are on a methodology row labeled "platinum cobalt visual comparison" methods.

The Capillary Ion Electrophoresis/Ultraviolet (CIE/UV) method, D6508, Rev. 2 has been moved from the ASTM column to the USGS/AOAC/Other column because this method is available from Waters Corporation (see footnote 54 in Table IB). This affects the following parameters: Bromide, mg/L; chloride, mg/L; fluoride—total, mg/L; nitrate (as N), mg/L; nitrite (as N), mg/L; orthophosphate (as P), mg/L; and sulfate (as SO₄) mg/L.

C. Changes to Table II

A time clarification of 15 minutes has been added to the parameter for Temperature.

The parameter 2-Chloroethylvinyl ether has been moved from the first row for Table IC organic tests to a separate row. Section 9.7 of the revised EPA Method 624.1 notes that acidification will destroy 2-chloroethylvinyl ether. Thus, adding HCl to pH 2 would not be acceptable for this parameter.

D. Change to Method Modifications and Analytical Requirements in § 136.6, Methods Modification Paragraph

For clarification purposes, the following two lines have been added to the methods modification paragraph (b): Where the laboratory is using a vendor-supplied method, it is the QC criteria in the reference method, not the vendor's method that must be met to show equivalency. Where a sample preparation step is required (*i.e.*, digestion, distillation), QC tests are to be run using standards treated in the same way as samples.

Also in this paragraph, the paragraph (b)(4)(xvi), "Changes are allowed in purge-and-trap sample volumes or operating conditions," was incorrectly deleted and is being reinstated.

Further, paragraph (b)(4)(xvii), regarding allowable modifications to Method 625, is being deleted as Method 625 has been replaced in its entirety with an updated version with this rulemaking.

E. Changes to EPA Method 608.3

EPA received numerous comments on Method 608.3, ranging from pointing out minor typographical errors to questioning substantive technical aspects of the proposed method. In response, EPA revised the method to address many of those comments. See the Response to Comments document available in the electronic docket listed in the **ADDRESSES** section at the beginning of this document for a detailed description of the changes.

Additionally, based on comments received in response to the proposal, EPA is reverting to the MDL values in the earlier version of Method 608 for those analytes that were included in Table 1 of Method 608.3. The MDLs in the proposed version of 608.3 were chosen for the proposed revision because they were determined with a capillary GC column. However, as noted by commenters, the values are not derived from a multiple laboratory validation study. Therefore, EPA has restored the original Method 608 MDL values. At such time as EPA develops new multi-laboratory MDL and ML values for the method, they will be included in a future revision and rulemaking.

Although EPA received comments about updating the QC acceptance criteria in Method 608.3, EPA did not adopt such changes because EPA lacks data from a multi-laboratory validation study from which to develop such criteria.

F. Change to EPA Method 611

In Section 1.1, EPA corrected the last parameter in the list of parameters table, that read "4-Chlorophenyl phenyl ether," a typographical error. The word "either" should be "ether." The correct parameter name is "4-Chlorophenyl phenyl ether."

G. Changes to EPA Method 624.1

EPA received numerous comments on Method 624.1, ranging from pointing out minor typographical errors to questioning substantive technical aspects of the proposed method. In response, EPA revised the method to address many of those comments. See the response to comments document available in the docket listed in the **ADDRESSES** section at the beginning of this document for a detailed description of the changes.

Additionally, section 8.1.2.1.2, subsection e, Sample matrices on which MS/MSD tests must be performed for nationwide use of an allowed modification, has been changed to update the web link for the list of industrial categories with existing effluent guidelines to <https://www.epa.gov/cwa-methods/alternate-test-procedure-documents>.

Although EPA received comments about updating the QC acceptance criteria in Method 624.1, EPA did not adopt such changes because EPA lacks data from a multi-laboratory validation study from which to develop such criteria.

H. Changes to EPA Method 625.1

EPA received numerous comments on Method 625.1, ranging from pointing out minor typographical errors to questioning substantive technical aspects of the proposed method. In response, EPA revised the method to address many of those comments. See the response to comments document available in the electronic docket listed in the **ADDRESSES** section at the beginning of this document for a detailed description of the changes.

Additionally, as was the case with EPA Method 624.1, section 8.1.2.1.2, subsection e, Sample matrices on which MS/MSD tests must be performed for nationwide use of an allowed modification, has been changed to update the web link for the list of industrial categories with existing effluent guidelines to <https://www.epa.gov/cwa-methods/alternate-test-procedure-documents>.

Although EPA received comments about updating the QC acceptance criteria in Method 625.1, EPA did not implement such changes because EPA

lacks data from a multi-laboratory validation study from which to develop such criteria.

I. Changes to Method Detection Limit (MDL) Procedure, Appendix B

No significant revisions were made to the proposed MDL procedure. Some flexibility was added to the procedure, as is discussed in Section II.K above.

J. Changes to WET Errata

Among the corrections that EPA proposed was a change to the language for Fathead minnows, Daphnids, and Green Alga in the document *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms*, Fourth Edition, U.S. Environmental Protection Agency, Office of Water, Washington, DC EPA/821/R-02/013, October 2002. For Fathead Minnows and Daphnids, EPA proposed to change "Conductivity, alkalinity, and hardness are measured in each new sample (100% effluent or receiving water) and in the control" to read "Conductivity, alkalinity, and hardness are measured at the beginning of the test for all test concentrations in each new sample and in the control before they are dispersed to the test chambers." EPA agrees with commenters that this change would constitute a change to the test rather than a correction or clarification. For that reason, EPA will not add the inserted language "at the beginning of the test for all test concentrations." EPA is retaining its deletion of "(100% effluent or receiving water)" and the insertion of "before they are dispensed to the test chamber" to the end of the sentence. Thus, the sentence will now read "Conductivity, alkalinity, and hardness are measured in each new sample and in the control before they are dispensed to the test chamber." For Green Alga, the proposed change has been eliminated from the errata because only the increased testing was proposed.

IV. Statutory and Executive Order Reviews

A. Executive Order 12866: Regulatory Planning and Review and Executive Order 13563: Improving Regulation and Regulatory Review

This rule is not a "significant regulatory action" under the terms of Executive Order (EO) 12866 (58 FR 51735, October 4, 1993) and is therefore not subject to review under EO 12866 and EO 13563.

B. Paperwork Reduction Act

This action does not impose an information collection burden under the provisions of the Paperwork Reduction

Act, 44 U.S.C. 3501 *et seq.* Burden is defined at 5 CFR 1320.3(b). This rule does not impose any information collection, reporting, or recordkeeping requirements. This rule merely adds new and revised versions of testing procedures, and sample preservation requirements.

C. Regulatory Flexibility Act

The Regulatory Flexibility Act (RFA) generally requires an agency to prepare a regulatory flexibility analysis of any rule subject to notice and comment rulemaking requirements under the Administrative Procedure Act or any other statute unless the agency certifies that the rule will not have a significant economic impact on a substantial number of small entities. Small entities include small businesses, small organizations, and small governmental jurisdictions.

For purposes of assessing the impacts of this rule on small entities for methods under the Clean Water Act, small entity is defined as: (1) A small business that meets RFA default definitions (based on SBA size standards) found in 13 CFR 121.201; (2) a small governmental jurisdiction that is a government of a city, county, town, school district or special district with a population less than 50,000; and (3) a small organization that is any not-for-profit enterprise which is independently owned and operated and is not dominant in its field.

After considering the economic impacts of this final rule on small entities, I certify that this action will not have a significant economic impact on a substantial number of small entities. This action approves new and revised versions of testing procedures. Generally, these changes will have a positive impact on small entities by increasing method flexibility, thereby allowing entities to reduce costs by choosing more cost-effective methods.

D. Unfunded Mandates Reform Act

This action contains no Federal mandates under the provisions of Title II of the Unfunded Mandates Reform Act of 1995 (UMRA), 2 U.S.C. 1531–1538 for State, local, or tribal governments, or the private sector.

EPA has determined that this final rule contains no regulatory requirements that might significantly or uniquely affect small governments. Generally, this action will have a positive impact by increasing method flexibility, thereby allowing method users to reduce costs by choosing more cost effective methods. In some cases, analytical costs may increase slightly due to changes in methods, but these

increases are neither significant, nor unique to small governments. This rule merely approves new and revised versions of testing procedures, and new sample collection, preservation, and holding time requirements.

Thus, this rule is not subject to the requirements of Section 203 of UMRA.

E. Executive Order 13132: Federalism

This final rule does not have federalism implications. It will not have substantial direct effects on the States, on the relationship between the national government and the States, or on the distribution of power and responsibilities among the various levels of government, as specified in Executive Order 13132 (64 FR 43255, Aug. 10, 1999). This rule merely approves new and revised versions of testing procedures, and new sample collection, preservation, and holding time requirements. The costs to State and local governments will be minimal. In fact, governments may see a cost savings because the rule adds flexibility for laboratories and permittees to choose between additional approved test methods and it also provides additional flexibility to modify existing test methods. Thus, laboratories and permittees will not make as many requests for approval of alternative test methods or method modifications, and the rule does not preempt State law. Thus, Executive Order 13132 does not apply to this rule.

In the spirit of Executive Order 13132, and consistent with EPA policy to promote communications between EPA and State and local governments, EPA specifically solicited comment on the proposed rule from State and local officials.

F. Executive Order 13175: Consultation and Coordination With Indian Tribal Governments

This final rule does not have tribal implications, as specified in Executive Order 13175, (65 FR 67249, Nov. 9, 2000). It will not have substantial direct effects on Tribal governments, on the relationship between the federal government and Indian tribes, or on the distribution of power and responsibilities between the federal government and Indian tribes. This rule merely approves new and revised versions of testing procedures, and new sample collection, preservation, and holding time requirements. The costs to tribal governments will be minimal. In fact, tribal governments may see a cost savings because the rule adds flexibility for laboratories and permittees to choose between additional approved test methods and it also provides additional

flexibility to modify existing test methods. Thus, laboratories and permittees will not make as many requests for approval of alternative test methods or method modifications. Thus, Executive Order 13175 does not apply to this rule.

In the spirit of Executive Order 13175, and consistent with EPA policy to promote communications between EPA and Indian tribes, EPA specifically solicited comment on the proposed rule from tribal officials. EPA did not receive any comments from Indian tribes.

G. Executive Order 13045: Protection of Children From Environmental Health Risks and Safety Risks

EPA interprets E.O. 13045 (62 FR 19885, April 23, 1997) as applying only to those regulatory actions that concern health or safety risks, such that the analysis required under section 5–501 of the E.O. has the potential to influence the regulation. This action is not subject to E.O. 13045 because it does not establish an environmental standard intended to mitigate health or safety risks. This rule approves new and revised versions of testing procedures, and new sample collection, preservation, and holding time requirements.

H. Executive Order 13211: Actions That Significantly Affect Energy Supply, Distribution, or Use

This action is not subject to Executive Order 13211, “Actions Concerning Regulations That Significantly Affect Energy Supply, Distribution, or Use” (66 FR 28355 (May 22, 2001)) because it is not a significant regulatory action under Executive Order 12866.

I. National Technology Transfer and Advancement Act of 1995

Section 12(d) of the National Technology Transfer and Advancement Act of 1995, (NTTAA), Public Law 104–113, section 12(d) (15 U.S.C. 272 note), directs EPA to use voluntary consensus standards in its regulatory activities unless to do so would be inconsistent with applicable law or otherwise impractical. Voluntary consensus standards are technical standards (e.g., material specifications, test methods, sampling procedures, and business practices) that are developed or adopted by voluntary consensus standard bodies. The NTTAA directs EPA to provide Congress, through the OMB, explanations when the Agency decides not to use available and applicable voluntary consensus standards.

This final rule approves the use of technical standards developed by the Standard Methods Committee, and

ASTM International for use in compliance monitoring where the Agency has determined that those standards meet the needs of Clean Water Act programs. EPA did not propose to add one Standard Method because that method had not undergone full inter-laboratory validation as recommended in current Agency guidance (see Section IV.C of the proposal for this rule (80 FR 8956, February 19, 2015)). All proposed voluntary consensus standards are approved in this rule.

J. Executive Order 12898: Federal Actions To Address Environmental Justice in Minority Populations and Low-Income Populations

Executive Order (E.O.) 12898 (59 FR 7629 (Feb. 16, 1994)) establishes federal executive policy on environmental justice. Its main provision directs federal agencies, to the greatest extent practicable and permitted by law, to make environmental justice part of their mission by identifying and addressing, as appropriate, disproportionately high and adverse human health or environmental effects of their programs, policies, and activities on minority populations and low-income populations in the United States.

This final rule provides additional compliance methods for use by any facility or laboratory with no disproportionate impact on minority or low-income populations because it merely approves new and revised versions of testing procedures to measure pollutants in water.

K. Congressional Review Act

The Congressional Review Act, 5 U.S.C. 801 *et seq.*, as added by the Small Business Regulatory Enforcement Fairness Act of 1996, generally provides that before a rule may take effect, the agency promulgating the rule must submit a rule report, which includes a copy of the rule, to each House of the Congress and to the Comptroller General of the United States. EPA will submit a report containing this rule and other required information to the U.S. Senate, the U.S. House of Representatives, and the Comptroller General of the United States prior to publication of the rule in the **Federal Register**. This action is not a “major rule” as defined by 5 U.S.C. 804(2). This rule will be effective September 27, 2017.

List of Subjects in 40 CFR Part 136

Environmental protection, Incorporation by reference, Reporting and recordkeeping requirements, Test procedures, Water pollution control.

Dated: August 7, 2017.

E. Scott Pruitt,

Administrator.

For the reasons set out in the preamble, title 40, chapter I of the Code of Federal Regulations is amended as follows:

**PART 136—GUIDELINES
ESTABLISHING TEST PROCEDURES
FOR THE ANALYSIS OF POLLUTANTS**

■ 1. The authority citation for part 136 continues to read as follows:

Authority: Secs. 301, 304(h), 307 and 501(a), Pub. L. 95–217, 91 Stat. 1566, *et seq.* (33 U.S.C. 1251, *et seq.*) (the Federal Water Pollution Control Act Amendments of 1972 as amended by the Clean Water Act of 1977).

■ 2. Section 136.1 is amended by revising paragraph (a) to read as follows:

§ 136.1 Applicability.

(a) The procedures prescribed herein shall, except as noted in §§ 136.4, 136.5, and 136.6, be used to perform the measurements indicated whenever the waste constituent specified is required to be measured for:

(1) An application submitted to the Director and/or reports required to be submitted under NPDES permits or other requests for quantitative or qualitative effluent data under parts 122 through 125 of this chapter; and

(2) Reports required to be submitted by dischargers under the NPDES established by parts 124 and 125 of this chapter; and

(3) Certifications issued by States pursuant to section 401 of the Clean Water Act (CWA), as amended.

* * * * *

■ 3. Section 136.2 is amended by revising paragraphs (d) and (f) to read as follows:

§ 136.2 Definitions.

* * * * *

(d) *Director* means the director as defined in 40 CFR 122.2.

* * * * *

(f) *Detection limit* means the minimum concentration of an analyte (substance) that can be measured and reported with a 99% confidence that the analyte concentration is distinguishable from the method blank results as determined by the procedure set forth at appendix B of this part.

■ 4. In § 136.3:

■ a. Revise paragraph (a) introductory text and tables IA, IB, IC, ID, IF, IG, and IH.

■ b. Revise paragraphs (b) introductory text, (b)(8)(iv), (b)(8)(v), (b)(8)(xiii), (b)(8)(xv), (b)(10)(viii) through (b)(10)(lxviii),

(b)(10)(lxi) through (b)(10)(lxiii), (b)(10)(lxviii), (b)(15)(v), (b)(15)(viii) through (x), (b)(15)(xii), (b)(15)(xiii), (b)(15)(xv) through (b)(15)(xvii), (b)(15)(xxii) through (b)(15)(xxiv), (b)(15)(xxx), (b)(15)(xxxv), (b)(15)(xxxvii), (b)(15)(xxxix), (b)(15)(xlii), (b)(15)(li), (b)(15)(lii), (b)(15)(lv), (b)(15)(lviii), (b)(15)(lix), (b)(15)(lxi), (b)(15)(lxiv), (b)(15)(lxvi), and (b)(15)(lxviii).

■ c. Redesignate paragraphs (b)(19)(vii) and (viii) as paragraphs (b)(19)(ix) and (x), respectively.

■ d. Add new paragraphs (b)(19)(vii) and (viii).

■ e. Revise paragraphs (b)(20)(i) through (iv).

■ f. Remove paragraph (b)(20)(v).

■ g. Revise paragraph (b)(25)(i).

■ h. Add paragraphs (b)(25)(ii) and (iii).

■ i. Redesignate paragraphs (b)(33) and (34) as paragraphs (b)(35) and (36), respectively, and redesignate paragraphs (b)(26) through (32) as paragraphs (b)(27) through (33), respectively.

■ j. Add new paragraphs (b)(26) and (34).

■ k. Revise newly redesignated paragraph (b)(35).

■ l. Revise paragraph (c) and Table II in paragraph (e).

The revisions and additions read as follows:

§ 136.3 Identification of test procedures.

(a) Parameters or pollutants, for which methods are approved, are listed together with test procedure descriptions and references in Tables IA, IB, IC, ID, IE, IF, IG, and IH of this section. The methods listed in Tables IA, IB, IC, ID, IE, IF, IG, and IH are incorporated by reference, see paragraph (b) of this section, with the exception of EPA Methods 200.7, 601–613, 624.1, 625.1, 1613, 1624, and 1625. The full texts of Methods 601–613, 624.1, 625.1, 1613, 1624, and 1625 are printed in appendix A of this part, and the full text of Method 200.7 is printed in appendix C of this part. The full text for determining the method detection limit when using the test procedures is given in appendix B of this part. In the event of a conflict between the reporting requirements of 40 CFR parts 122 and 125 and any reporting requirements associated with the methods listed in these tables, the provisions of 40 CFR parts 122 and 125 are controlling and will determine a permittee’s reporting requirements. The full texts of the referenced test procedures are incorporated by reference into Tables IA, IB, IC, ID, IE, IF, IG, and IH. The year after the method number indicates the latest editorial change of the method. The discharge parameter values for which reports are required must be

determined by one of the standard analytical test procedures incorporated by reference and described in Tables IA, IB, IC, ID, IE, IF, IG, and IH or by any

alternate test procedure which has been approved by the Administrator under the provisions of paragraph (d) of this section and §§ 136.4 and 136.5. Under

certain circumstances (paragraph (c) of this section, in § 136.5(a) through (d) or 40 CFR 401.13) other additional or alternate test procedures may be used.

TABLE IA—LIST OF APPROVED BIOLOGICAL METHODS FOR WASTEWATER AND SEWAGE SLUDGE

Parameter and units	Method ¹	EPA	Standard methods	AOAC, ASTM, USGS	Other
Bacteria					
1. Coliform (fecal), number per 100 mL or number per gram dry weight.	Most Probable Number (MPN), 5 tube, 3 dilution, or. Multiple tube/multiple well, or. Membrane filter (MF) ² , single step.	p. 132, ³ 1680, ^{11 15} 1681 ^{11 20} .	9221 C E–2006.		
2. Coliform (fecal) in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or. MF ² , single step ⁵	p. 124 ³ p. 124 ³	9222 D–2006 ³⁰ 9222 D–2006 ³⁰ .	B–0050–85 ⁴ .	
3. Coliform (total), number per 100 mL	MPN, 5 tube, 3 dilution, or. MF ² , single step or two step.	p. 114 ³ p. 108 ³	9221 B–2006. 9222 B–2006	B–0025–85 ⁴ .	
4. Coliform (total), in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or. MF ² with enrichment ⁵ .	p. 114 ³ p. 111 ³	9221 B–2006. 9222 B–2006.		
5. <i>E. coli</i> , number per 100 mL ²¹	MPN ^{6 8 16} multiple tube, or. multiple tube/multiple well, or. MF ^{2 6 7 8} single step 1603 ²²	9221B.2–2006/ 9221F–2006 ^{12 14} . 9223 B–2004 ¹³	991.15 ¹⁰	Colilert® ^{13 18} . Colilert-18® ^{13 17 18} mColiBlue-24® ¹⁹ .
6. Fecal streptococci, number per 100 mL	MPN, 5 tube, 3 dilution, or. MF ² , or	p. 139 ³ p. 136 ³	9230 B–2007. 9230 C–2007	B–0055–85 ⁴	
7. Enterococci, number per 100 mL ²¹	Plate count	p. 143 ³ .			
	MPN, 5 tube, 3 dilution, or. MPN ^{6 8} , multiple tube/multiple well, or. MF ^{2 6 7 8} single step or. Plate count	p. 139 ³ 1600 ²⁵ p. 143 ³ .	9230 B–2007		
8. <i>Salmonella</i> number per gram dry weight ¹¹	MPN multiple tube	1682 ²³ .	9230 D–2007 9230 C–2007.	D6503–99 ⁹	Enterolert® ^{13 24} .
Aquatic Toxicity					
9. Toxicity, acute, fresh water organisms, LC ₅₀ , percent effluent.	<i>Ceriodaphnia dubia</i> acute. <i>Daphnia pulex</i> and <i>Daphnia magna</i> acute. Fathead Minnow, <i>Pimephales promelas</i> , and Bannerfin shiner, <i>Cyprinella leedsii</i> , acute. Rainbow Trout, <i>Oncorhynchus mykiss</i> , and brook trout, <i>Salvelinus fontinalis</i> , acute.	2002.0 ²⁶ . 2021.0 ²⁶ . 2000.0 ²⁶ . 2019.0 ²⁶ .			
10. Toxicity, acute, estuarine and marine organisms of the Atlantic Ocean and Gulf of Mexico, LC ₅₀ , percent effluent.	Mysid, <i>Mysidopsis bahia</i> , acute. Sheepshead Minnow, <i>Cyprinodon variegatus</i> , acute. Siverside, <i>Menidia beryllina</i> , <i>Menidia menidia</i> , and <i>Menidia peninsulae</i> , acute.	2007.0 ²⁶ . 2004.0 ²⁶ . 2006.0 ²⁶ .			
11. Toxicity, chronic, fresh water organisms, NOEC or IC ₂₅ , percent effluent.	Fathead minnow, <i>Pimephales promelas</i> , larval survival and growth.	1000.0 ²⁷ .			

TABLE IA—LIST OF APPROVED BIOLOGICAL METHODS FOR WASTEWATER AND SEWAGE SLUDGE—Continued

Parameter and units	Method ¹	EPA	Standard methods	AOAC, ASTM, USGS	Other
12. Toxicity, chronic, estuarine and marine organisms of the Atlantic Ocean and Gulf of Mexico, NOEC or IC ₂₅ , percent effluent.	Fathead minnow, <i>Pimephales promelas</i> , embryo-larval survival and teratogenicity.	1001.0 ²⁷ .			
	Daphnia, <i>Ceriodaphnia dubia</i> , survival and reproduction.	1002.0 ²⁷ .			
	Green alga, <i>Selenastrum capricornutum</i> , growth.	1003.0 ²⁷ .			
	Sheepshead minnow, <i>Cyprinodon variegatus</i> , larval survival and growth.	1004.0 ²⁸ .			
	Sheepshead minnow, <i>Cyprinodon variegatus</i> , embryo-larval survival and teratogenicity.	1005.0 ²⁸ .			
	Inland silverside, <i>Menidia beryllina</i> , larval survival and growth.	1006.0 ²⁸ .			
	Mysid, <i>Mysidopsis bahia</i> , survival, growth, and fecundity.	1007.0 ²⁸ .			
	Sea urchin, <i>Arbacia punctulata</i> , fertilization.	1008.0 ²⁸ .			

Table IA notes:

¹ The method must be specified when results are reported.

² A 0.45-μm membrane filter (MF) or other pore size certified by the manufacturer to fully retain organisms to be cultivated and to be free of extractables which could interfere with their growth.

³ Microbiological Methods for Monitoring the Environment, Water, and Wastes, EPA/600/8-78/017. 1978. U.S. EPA.

⁴ U.S. Geological Survey Techniques of Water-Resource Investigations, Book 5, Laboratory Analysis, Chapter A4, Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples. 1989. USGS.

⁵ Because the MF technique usually yields low and variable recovery from chlorinated wastewaters, the Most Probable Number method will be required to resolve any controversies.

⁶ Tests must be conducted to provide organism enumeration (density). Select the appropriate configuration of tubes/filtrations and dilutions/volumes to account for the quality, character, consistency, and anticipated organism density of the water sample.

⁷ When the MF method has been used previously to test waters with high turbidity, large numbers of noncoliform bacteria, or samples that may contain organisms stressed by chlorine, a parallel test should be conducted with a multiple-tube technique to demonstrate applicability and comparability of results.

⁸ To assess the comparability of results obtained with individual methods, it is suggested that side-by-side tests be conducted across seasons of the year with the water samples routinely tested in accordance with the most current Standard Methods for the Examination of Water and Wastewater or EPA alternate test procedure (ATP) guidelines.

⁹ Annual Book of ASTM Standards-Water and Environmental Technology, Section 11.02. 2000, 1999, 1996. ASTM International.

¹⁰ Official Methods of Analysis of AOAC International. 16th Edition, 4th Revision, 1998. AOAC International.

¹¹ Approved for enumeration of target organism in sewage sludge.

¹² The multiple-tube fermentation test is used in 9221B.2-2006. Lactose broth may be used in lieu of lauryl tryptose broth (LTB), if at least 25 parallel tests are conducted between this broth and LTB using the water samples normally tested, and this comparison demonstrates that the false-positive rate and false-negative rate for total coliform using lactose broth is less than 10 percent. No requirement exists to run the completed phase on 10 percent of all total coliform-positive tubes on a seasonal basis.

¹³ These tests are collectively known as defined enzyme substrate tests, where, for example, a substrate is used to detect the enzyme β-glucuronidase produced by *E. coli*.

¹⁴ After prior enrichment in a presumptive medium for total coliform using 9221B.2-2006, all presumptive tubes or bottles showing any amount of gas, growth or acidity within 48 h ± 3 h of incubation shall be submitted to 9221F-2006. Commercially available EC-MUG media or EC media supplemented in the laboratory with 50 μg/mL of MUG may be used.

¹⁵ Method 1680: Fecal Coliforms in Sewage Sludge (Biosolids) by Multiple-Tube Fermentation Using Lauryl-Tryptose Broth (LTB) and EC Medium, EPA-821-R-14-009. September 2014. U.S. EPA.

¹⁶ Samples shall be enumerated by the multiple-tube or multiple-well procedure. Using multiple-tube procedures, employ an appropriate tube and dilution configuration of the sample as needed and report the Most Probable Number (MPN). Samples tested with Colilert® may be enumerated with the multiple-well procedures, Quanti-Tray® and the MPN calculated from the table provided by the manufacturer.

¹⁷ Colilert-18® is an optimized formulation of the Colilert® for the determination of total coliforms and *E. coli* that provides results within 18 h of incubation at 35°C rather than the 24 h required for the Colilert® test and is recommended for marine water samples.

¹⁸ Descriptions of the Colilert®, Colilert-18®, and Quanti-Tray® may be obtained from IDEXX Laboratories, Inc.

¹⁹ A description of the mColiBlue24® test, is available from Hach Company.

²⁰ Method 1681: Fecal Coliforms in Sewage Sludge (Biosolids) by Multiple-Tube Fermentation using A-1 Medium, EPA-821-R-06-013. July 2006. U.S. EPA.

²¹ Approved for enumeration of target organism in wastewater effluent.

²² Method 1603: *Escherichia coli* (*E. coli*) in Water by Membrane Filtration Using Modified membrane-Thermotolerant *Escherichia coli* Agar (modified mTEC), EPA-821-R-14-010. September 2014. U.S. EPA.

²³ Method 1682: *Salmonella* in Sewage Sludge (Biosolids) by Modified Semisolid Rappaport-Vassiliadis (MSRV) Medium, EPA-821-R-14-012. September 2014. U.S. EPA.

²⁴ A description of the Enterolert® test may be obtained from IDEXX Laboratories Inc.

²⁵ Method 1600: Enterococci in Water by Membrane Filtration Using membrane-Enterococcus Indoxyl-β-D-Glucoside Agar (mEI), EPA-821-R-14-011. September 2014. U.S. EPA.

²⁶ Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, EPA-821-R-02-012. Fifth Edition, October 2002. U.S. EPA.

²⁷ Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, EPA-821-R-02-013. Fourth Edition, October 2002. U.S. EPA.

²⁸ Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, EPA-821-R-02-014. Third Edition, October 2002. U.S. EPA.

²⁹ To use Colilert-18® to assay for fecal coliforms, the incubation temperature is 44.5 ± 0.2 °C, and a water bath incubator is used.

³⁰ On a monthly basis, at least ten blue colonies from the medium must be verified using Lauryl Tryptose Broth and EC broth, followed by count adjustment based on these results; and representative non-blue colonies should be verified using Lauryl Tryptose Broth. Where possible, verifications should be done from randomized sample sources.

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter	Methodology ⁵⁸	EPA ⁵²	Standard methods	ASTM	USGS/AOAC/other
1. Acidity, as CaCO ₃ , mg/L.	Electrometric endpoint or phenolphthalein endpoint.	2310 B–2011	D1067–11	I–1020–85. ²
2. Alkalinity, as CaCO ₃ , mg/L.	Electrometric or Colorimetric titration to pH 4.5, Manual.	2320 B–2011	D1067–11	973.43, ³ I–1030–85. ²
3. Aluminum—Total, ⁴ mg/L.	Automatic	310.2 (Rev. 1974) ¹	I–2030–85. ²
	Digestion, ⁴ followed by any of the following: AA direct aspiration ³⁶	3111 D–2011 or 3111 E–2011. 3113 B–2010.	I–3051–85. ²
	AA furnace
	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES ³⁶	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
	Direct Current Plasma (DCP) ³⁶	D4190–08	See footnote. ³⁴
	Colorimetric (Eriochrome cyanine R).	3500-Al B–2011.
	Manual distillation ⁶ or gas diffusion (pH > 11), followed by any of the following: Nesslerization	350.1, Rev. 2.0 (1993) ...	4500–NH ₃ B–2011	973.49. ³
	Titration	4500–NH ₃ C–2011.	D1426–08 (A)	973.49, ³ I–3520–85. ²
4. Ammonia (as N), mg/L	Electrode	4500–NH ₃ D–2011 or E–2011.	D1426–08 (B).
	Manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.	4500–NH ₃ F–2011	See footnote. ⁶⁰
	Automated phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.	350.1, ³⁰ Rev. 2.0 (1993)	4500–NH ₃ G–2011, 4500–NH ₃ H–2011.	I–4523–85. ²
	Automated electrode	See footnote. ⁷
	Ion Chromatography	D6919–09.
	Automated gas diffusion, followed by conductivity cell analysis.	Timberline Ammonia-001. ⁷⁴
	Digestion, ⁴ followed by any of the following: AA direct aspiration ³⁶	3111 B–2011. 3113 B–2010.
	AA furnace
	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES ³⁶	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
5. Antimony—Total, ⁴ mg/L	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
	Digestion, ⁴ followed by any of the following: AA gaseous hydride	206.5 (Issued 1978) ¹
	3114 B–2011 or 3114 C–2011.	D2972–08 (B)	I–3062–85. ²
	AA furnace	3113 B–2010	D2972–08 (C)	I–4063–98. ⁴⁹
	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES ³⁶	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12.
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4020–05. ⁷⁰
	Colorimetric (SDDC)	3500-As B–2011	D2972–08 (A)	I–3060–85. ²
	Digestion, ⁴ followed by any of the following: AA direct aspiration ³⁶	3111 D–2011	I–3084–85. ²
	AA furnace	3113 B–2010	D4382–12.
6. Arsenic—Total, ⁴ mg/L	ICP/AES ³⁶	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
	DCP ³⁶	See footnote. ³⁴
	Digestion, ⁴ followed by any of the following: AA direct aspiration	3111 D–2011 or 3111 E–2011.	D3645–08 (A)	I–3095–85. ²
	AA furnace	3113 B–2010	D3645–08 (B).
	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
	DCP ³⁶	See footnote. ³⁴
	Digestion, ⁴ followed by any of the following: AA direct aspiration	3111 D–2011 or 3111 E–2011.	D3645–08 (A)	I–3095–85. ²
7. Barium—Total, ⁴ mg/L	AA furnace	3113 B–2010	D3645–08 (B).
	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES ³⁶	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
	DCP ³⁶	See footnote. ³⁴
	Digestion, ⁴ followed by any of the following: AA direct aspiration	3111 D–2011 or 3111 E–2011.	D3645–08 (A)	I–3095–85. ²
	AA furnace	3113 B–2010	D3645–08 (B).
	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
8. Beryllium—Total, ⁴ mg/L	DCP ³⁶	See footnote. ³⁴
	Digestion, ⁴ followed by any of the following: AA direct aspiration	3111 D–2011 or 3111 E–2011.	D3645–08 (A)	I–3095–85. ²
	AA furnace	3113 B–2010	D3645–08 (B).
	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
	DCP ³⁶	See footnote. ³⁴
	Digestion, ⁴ followed by any of the following: AA direct aspiration	3111 D–2011 or 3111 E–2011.	D3645–08 (A)	I–3095–85. ²
	AA furnace	3113 B–2010	D3645–08 (B).
	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology ⁵⁸	EPA ⁵²	Standard methods	ASTM	USGS/AOAC/other
9. Biochemical oxygen demand (BOD ₅), mg/L. 10. Boron—Total, ³⁷ mg/L	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B—2011	D5673–10	993.14, ³ I–4471–97, ⁵⁰ See footnote. ³⁴
	DCP	D4190–08
	Colorimetric (aluminon)	See footnote. ⁶¹
	Dissolved Oxygen Depletion.	5210 B—2011	973.44, ³ p. 17, ⁹ I–1578–78, ⁸ See footnote. ^{10 63}
11. Bromide, mg/L	Colorimetric (curcumin)	4500-B B—2011	I–3112–85. ²
	ICP/AES	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B—2011	D1976–12	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B—2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
	DCP	D4190–08	See footnote. ³⁴
12. Cadmium—Total, ⁴ mg/L.	Electrode	D1246–10	I–1125–85. ²
	Ion Chromatography	300.0, Rev. 2.1 (1993) and 300.1, Rev. 1.0 (1997).	4110 B—2011, C—2011, D—2011.	D4327–03	993.30. ³
	CIE/UV	4140 B—2011	D6508–10	D6508, Rev. 2. ⁵⁴
	Digestion, ⁴ followed by any of the following: AA direct aspiration ³⁶	3111 B—2011 or 3111 C—2011.	D3557–12 (A or B)	974.27, ³ p. 37, ⁹ I–3135–85 ² or I–3136–85. ²
13. Calcium—Total, ⁴ mg/L	AA furnace	3113 B—2010	D3557–12 (D)	I–4138–89. ⁵¹
	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES ³⁶	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B—2011	D1976–12	I–1472–85. ² or I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B—2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
	DCP ³⁶	D4190–08	See footnote. ³⁴
	Voltametry ¹¹	D3557–12 (C).
	Colorimetric (Dithizone)	3500-Cd-D-1990.
	Digestion, ⁴ followed by any of the following: AA direct aspiration	3111 B—2011	D511–09(B)	I–3152–85. ²
	ICP/AES	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B—2011	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B—2011	D5673–10	993.14, ³
14. Carbonaceous biochemical oxygen demand (CBOD ₅), mg/L ¹² .	DCP	D4190–08	See footnote. ³⁴
	Titrimetric (EDTA)	3500-Ca B—2011	D511–09 (A).
	Ion Chromatography	D6919–09.
	Dissolved Oxygen Depletion with nitrification inhibitor.	5210 B—2011	See footnote. ^{35 63}
15. Chemical oxygen demand (COD), mg/L.	Titrimetric	410.3 (Rev. 1978) ¹	5220 B—2011 or C—2011	D1252–06 (A)	973.46, ³ p. 17, ⁹ I–3560–85. ²
	Spectrophotometric, manual or automatic.	410.4, Rev. 2.0 (1993) ...	5220 D—2011	D1252–06 (B)	See footnotes. ^{13 14} , I–3561–85. ²
16. Chloride, mg/L	Titrimetric: (silver nitrate)	4500-Cl– B—2011	D512–04 (B)	I–1183–85. ²
	(Mercuric nitrate)	4500-Cl– C—2011	D512–04 (A)	973.51, ³ I–1184–85. ²
	Colorimetric: Manual	I–1187–85. ²
	Automated (ferricyanide)	4500-Cl– E—2011	I–2187–85. ²
	Potentiometric Titration	4500-Cl– D—2011.
	Ion Selective Electrode	D512–04 (C).
	Ion Chromatography	300.0, Rev. 2.1 (1993) and 300.1, Rev. 1.0 (1997).	4110 B—2011 or 4110 C—2011.	D4327–03	993.30, ³ I–2057–90. ⁵¹
	CIE/UV	4140 B—2011	D6508–10	D6508, Rev. 2. ⁵⁴
	Amperometric direct	4500-Cl D—2011	D1253–08.
	Amperometric direct (low level).	4500-Cl E—2011.
17A. Chlorine-Free Available, mg/L.	Iodometric direct	4500-Cl B—2011.
	Back titration ether endpoint ¹⁵	4500-Cl C—2011.
	DPD–FAS	4500-Cl F—2011.
	Spectrophotometric, DPD	4500-Cl G—2011.
	Electrode	See footnote. ¹⁶
	Amperometric direct	4500-Cl D—2011	D1253–08.
	Amperometric direct (low level).	4500-Cl E—2011.
	DPD–FAS	4500-Cl F—2011.
	Spectrophotometric, DPD	4500-Cl G—2011.
	0.45-micron filtration followed by any of the following: AA chelation-extraction	3111 C—2011	I–1232–85. ²
18. Chromium VI dissolved, mg/L.	Ion Chromatography	218.6, Rev. 3.3 (1994) ...	3500-Cr C—2011	D5257–11	993.23. ³
	Colorimetric (diphenyl-carbazide).	3500-Cr B—2011	D1687–12 (A)	I–1230–85. ²
	Digestion, ⁴ followed by any of the following: AA direct aspiration ³⁶	3111 B—2011	D1687–12 (B)	974.27, ³ I–3236–85. ²
	AA chelation-extraction	3111 C—2011.
19. Chromium—Total, ⁴ mg/L.	AA furnace	3113 B—2010	D1687–12 (C)	I–3233–93. ⁴⁶

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology ⁵⁸	EPA ⁵²	Standard methods	ASTM	USGS/AOAC/other
20. Cobalt—Total, ⁴ mg/L	STGFAA	200.9, Rev. 2.2 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/AES ³⁶	200.5, Rev 4.2 (2003); ⁶⁸			
	ICP/MS	200.7, Rev. 4.4 (1994).			
	DCP ³⁶	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4020–05. ⁷⁰
	Colorimetric (diphenyl-carbazide).	3500-Cr B–2011.	D4190–08	
	Digestion, ⁴ followed by any of the following:
21. Color, platinum cobalt units or dominant wavelength, hue, luminance purity.	AA direct aspiration	3111 B–2011 or 3111 C–2011.	D3558–08 (A or B)	p. 37, ⁹ I–3239–85. ²
	AA furnace	3113 B–2010	D3558–08 (C)	I–4243–89. ⁵¹
	STGFAA	200.9, Rev. 2.2 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/AES ³⁶	200.5, Rev 4.2 (2003); ⁶⁸			
	ICP/MS	200.7, Rev. 4.4 (1994) ...			
	DCP	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4020–05. ⁷⁰
22. Copper—Total, ⁴ mg/L	Colorimetric (ADMI)	2120 F–2011 ⁷⁸ .	D4190–08	
	Platinum cobalt visual comparison.	2120 B–2011	I–1250–85. ²
	Spectrophotometric	See footnote. ¹⁸
	Digestion, ⁴ followed by any of the following:
	AA direct aspiration ³⁶	3111 B–2011 or 3111 C–2011.	D1688–12 (A or B)	974.27, ³ p. 37, ⁹ I–3270–85 ² or I–3271–85. ²
	AA furnace	3113 B–2010	D1688–12 (C)	I–4274–89. ⁵¹
23. Cyanide—Total, mg/L	STGFAA	200.9, Rev. 2.2 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/AES ³⁶	200.5, Rev 4.2 (2003); ⁶⁸			
	ICP/MS	200.7, Rev. 4.4 (1994).			
	DCP ³⁶	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4020–05. ⁷⁰
	Colorimetric (Neocuproine).	3500-Cu B–2011.	D4190–08	
	Colorimetric (Bathocuproine).	3500-Cu C–2011	See footnote. ¹⁹
	Automated UV digestion/distillation and Colorimetry.	Kelada-01. ⁵⁵
	Segmented Flow Injection, In-Line Ultraviolet Digestion, followed by gas diffusion amperometry.	D7511–12.
	Manual distillation with MgCl ₂ , followed by any of the following:	335.4, Rev. 1.0 (1993) ⁵⁷	4500-CN [−] B–2011 and C–2011.	D2036–09(A), D7284–13	10–204–00–1–X. ⁵⁶
	Flow Injection, gas diffusion amperometry.	D2036–09(A) D7284–13.
	Titrimetric	4500-CN [−] D–2011	D2036–09(A)	p. 22. ⁹
	Spectrophotometric, manual.	4500-CN [−] E–2011	D2036–09(A)	I–3300–85. ²
24. Cyanide—Available, mg/L.	Semi-Automated ²⁰	335.4, Rev. 1.0 (1993) ⁵⁷	10–204–00–1–X, ⁵⁶ I–4302–85. ²
	Ion Chromatography	D2036–09(A).
	Ion Selective Electrode	4500-CN [−] F–2011	D2036–09(A).
	Cyanide Amenable to Chlorination (CATC); Manual distillation with MgCl ₂ , followed by Titrimetric or Spectrophotometric.	4500-CN [−] G–2011	D2036–09(B).
	Flow injection and ligand exchange, followed by gas diffusion amperometry ⁵⁹	D6888–09	OIA–1677–09. ⁴⁴
	Automated Distillation and Colorimetry (no UV digestion).	Kelada-01. ⁵⁵
24.A Cyanide—Free, mg/L.	Flow Injection, followed by gas diffusion amperometry.	D7237–10	OIA–1677–09. ⁴⁴
	Manual micro-diffusion and colorimetry.	D4282–02.
25. Fluoride—Total, mg/L	Manual distillation, ⁶ followed by any of the following:	4500-F [−] B–2011.
	Electrode, manual	4500-F [−] C–2011	D1179–10 (B).
	Electrode, automated	4500-F [−] D–2011	D1179–10 (A).	I–4327–85. ²
	Colorimetric, (SPADNS)

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology ⁵⁸	EPA ⁵²	Standard methods	ASTM	USGS/AOAC/other
26. Gold—Total, ⁴ mg/L	Automated complexone .. Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1, Rev 1.0 (1997).	4500-F ⁻ E-2011. 4110 B-2011 or C-2011	D4327-03	993.30. ³
	CIE/UV		4140 B-2011	D6508-10	D6508, Rev. 2. ⁵⁴
	Digestion, ⁴ followed by any of the following:				
	AA direct aspiration		3111 B-2011.		
27. Hardness—Total, as CaCO ₃ , mg/L.	AA furnace	231.2 (Issued 1978) ¹	3113 B-2010.		
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B-2011	D5673-10	993.14. ³
	DCP				See footnote. ³⁴
	Automated colorimetric ...	130.1 (Issued 1971) ¹ .			
28. Hydrogen ion (pH), pH units.	Titrimetric (EDTA)		2340 C-2011	D1126-12	973.52B, ³ I-1338-85. ²
	Ca plus Mg as their car- bonates, by any ap- proved method for Ca and Mg (See Param- eters 13 and 33), pro- vided that the sum of the lowest point of quantitation for Ca and Mg is below the NPDES permit require- ment for Hardness..		2340 B-2011.		
	Electrometric measure- ment.		4500-H ⁺ B-2011	D1293-99 (A or B)	973.41, ³ I-1586-85. ²
	Automated electrode	150.2 (Dec. 1982) ¹			See footnote, ²¹ I-2587- 85. ²
29. Iridium—Total, ⁴ mg/L	Digestion, ⁴ followed by any of the following:				
	AA direct aspiration		3111 B-2011.		
	AA furnace	235.2 (Issued 1978) ¹ .			
	ICP/MS		3125 B-2011.		
30. Iron—Total, ⁴ mg/L	Digestion, ⁴ followed by any of the following:				
	AA direct aspiration ³⁶ ...		3111 B-2011 or 3111 C- 2011.	D1068-10 (A)	974.27, ³ I-3381-85. ²
	AA furnace		3113 B-2010	D1068-10 (B).	
	STGFAA	200.9, Rev. 2.2 (1994).			
31. Kjeldahl Nitrogen ⁵ — Total, (as N), mg/L.	ICP/AES ³⁶	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B-2011	D1976-12	I-4471-97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B-2011	D5673-10	993.14. ³
	DCP ³⁶			D4190-08	See footnote. ³⁴
	Colorimetric (Phenan- throlene).		3500-Fe B-2011	D1068-10 (C)	See footnote. ²²
	Manual digestion ²⁰ and distillation or gas diffu- sion, followed by any of the following:.		4500-N _{org} B-2011 or C- 2011 and 4500-NH ₃ B-2011.	D3590-11 (A)	I-4515-91. ⁴⁵
	Titration		4500-NH ₃ C-2011		973.48. ³
	Nesslerization			D1426-08 (A).	
	Electrode		4500-NH ₃ D-2011 or E- 2011.	D1426-08 (B).	
	Semi-automated phenate	350.1, Rev. 2.0 (1993) ...	4500-NH ₃ G-2011 4500- NH ₃ H-2011.		
	Manual phenate, salicy- late, or other sub- stituted phenols in Berthelot reaction based methods.		4500-NH ₃ F-2011		See footnote. ⁶⁰
	Automated gas diffusion, followed by conduc- tivity cell analysis.				Timberline Ammonia- 001. ⁷⁴
Automated Methods for TKN that do not require manual distillation.					
	Automated phenate, sali- cyate, or other sub- stituted phenols in Berthelot reaction based methods colori- metric (auto digestion and distillation).	351.1 (Rev. 1978) ¹			I-4551-78. ⁸
	Semi-automated block digestor colorimetric (distillation not re- quired).	351.2, Rev. 2.0 (1993) ...	4500-N _{org} D-2011	D3590-11 (B)	I-4515-91. ⁴⁵
	Block digester, followed by Auto distillation and Titration.				See footnote. ³⁹

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology ⁵⁸	EPA ⁵²	Standard methods	ASTM	USGS/AOAC/other
32. Lead—Total, ⁴ mg/L ...	Block digester, followed by Auto distillation and Nesslerization.	See footnote. ⁴⁰
	Block Digester, followed by Flow injection gas diffusion (distillation not required).	See footnote. ⁴¹
	Digestion with peroxodisulfate, followed by Spectrophotometric (2,6-dimethyl phenol).	Hach 10242. ⁷⁶
	Digestion with persulfate, followed by Colorimetric.	NCASI TNTP W10900. ⁷⁷
	Digestion, ⁴ followed by any of the following:
	AA direct aspiration ³⁶	3111 B–2011 or 3111 C–2011.	D3559–08 (A or B)	974.27, ³ I–3399–85. ²
	AA furnace	3113 B–2010	D3559–08 (D)	I–4403–89. ⁵¹
33. Magnesium—Total, ⁴ mg/L.	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES ³⁶	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
	DCP ³⁶	D4190–08	See footnote. ³⁴
	Voltametry ¹¹	D3559–08 (C).
	Colorimetric (Dithizone)	3500-Pb B–2011.
	Digestion, ⁴ followed by any of the following:
34. Manganese—Total, ⁴ mg/L.	AA direct aspiration	3111 B–2011	D511–09 (B)	974.27, ³ I–3447–85. ²
	ICP/AES	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³
	DCP	See footnote. ³⁴
	Ion Chromatography	D6919–09.
	Digestion, ⁴ followed by any of the following:
	AA direct aspiration ³⁶	3111 B–2011	D858–12 (A or B)	974.27, ³ I–3454–85. ²
35. Mercury—Total, ⁴ mg/L	AA furnace	3113 B–2010	D858–12 (C).
	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES ³⁶	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
	DCP ³⁶	D4190–08	See footnote. ³⁴
	Colorimetric (Persulfate)	3500-Mn B–2011	920.203. ³
	Colorimetric (Periodate)	See footnote. ²³
36. Molybdenum—Total, ⁴ mg/L.	Cold vapor, Manual	245.1, Rev. 3.0 (1994) ...	3112 B–2011	D3223–12	977.22, ³ I–3462–85. ²
	Cold vapor, Automated ..	245.2 (Issued 1974) ¹
	Cold vapor atomic fluorescence spectrometry (CVAFS).	245.7 Rev. 2.0 (2005) ¹⁷	I–4464–01. ⁷¹
	Purge and Trap CVAFS	1631E ⁴³
	Digestion, ⁴ followed by any of the following:
	AA direct aspiration	3111 D–2011	I–3490–85. ²
	AA furnace	3113 B–2010	I–3492–96. ⁴⁷
37. Nickel—Total, ⁴ mg/L	ICP/AES ³⁶	200.7, Rev. 4.4 (1994) ...	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4471–97. ⁵⁰
	DCP	See footnote. ³⁴
	Digestion, ⁴ followed by any of the following:
	AA direct aspiration ³⁶	3111 B–2011 or 3111 C–2011.	D1886–08 (A or B)	I–3499–85. ²
	AA furnace	3113 B–2010	D1886–08 (C)	I–4503–89. ⁵¹
	STGFAA	200.9, Rev. 2.2 (1994).
38. Nitrate (as N), mg/L ...	ICP/AES ³⁶	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I–4020–05. ⁷⁰
	DCP ³⁶	D4190–08	See footnote. ³⁴
	Ion Chromatography	300.0, Rev. 2.1 (1993) and 300.1, Rev. 1.0 (1997).	4110 B–2011 or C–2011	D4327–03	993.30. ³
	CIE/UV	4140 B–2011	D6508–10	D6508, Rev. 2. ⁵⁴
	Ion Selective Electrode	4500–NO ₃ [–] D–2011.	973.50, ³ 419D1, ⁷ p. 28. ⁹
	Colorimetric (Brucine sulfate).	352.1 (Issued 1971) ¹	Hach 10206. ⁷⁵
39. Nitrate-nitrite (as N), mg/L.	Spectrophotometric (2,6-dimethylphenol).
	Nitrate-nitrite N minus Nitrite N (See parameters 39 and 40).
	Cadmium reduction, Manual.	4500–NO ₃ [–] E–2011	D3867–04 (B).

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology ⁵⁸	EPA ⁵²	Standard methods	ASTM	USGS/AOAC/other
40. Nitrite (as N), mg/L	Cadmium reduction, Automated.	353.2, Rev. 2.0 (1993) ...	4500-NO ₃ - F-2011	D3867-04 (A)	I-2545-90. ⁵¹
	Automated hydrazine	4500-NO ₃ - H-2011.
	Reduction/Colorimetric	See footnote. ⁶²
	Ion Chromatography	300.0, Rev. 2.1 (1993) and 300.1, Rev. 1.0 (1997).	4110 B-2011 or C-2011	D4327-03	993.30. ³
	CIE/UV	4140 B-2011	D6508-10	D6508, Rev. 2. ⁵⁴
	Enzymatic reduction, followed by automated colorimetric determination.	I-2547-11, ⁷² I-2548-11, ⁷² N07-0003. ⁷³
	Spectrophotometric (2,6-dimethylphenol).	Hach 10206. ⁷⁵
	Spectrophotometric: Manual.	4500-NO ₂ - B-2011	See footnote. ²⁵
	Automated (Diazotization).	I-4540-85, ² See footnote. ⁶²
	Automated (*bypass cadmium reduction).	353.2, Rev. 2.0 (1993) ...	4500-NO ₃ - F-2011	D3867-04 (A)	I-4545-85. ²
41. Oil and grease—Total recoverable, mg/L.	Manual (*bypass cadmium reduction).	4500-NO ₃ - E-2011	D3867-04 (B).
	Ion Chromatography	300.0, Rev. 2.1 (1993) and 300.1, Rev. 1.0 (1997).	4110 B-2011 or C-2011	D4327-03	993.30. ³
	CIE/UV	4140 B-2011	D6508-10	D6508, Rev. 2. ⁵⁴
	Automated (*bypass Enzymatic reduction).	I-2547-11, ⁷² I-2548-11, ⁷² N07-0003. ⁷³
42. Organic carbon—Total (TOC), mg/L.	Hexane extractable material (HEM): n-Hexane extraction and gravimetry.	1664 Rev. A; 1664 Rev. B ⁴² .	5520 B-2011 ³⁸
	Silica gel treated HEM (SGT-HEM): Silica gel treatment and gravimetry.	1664 Rev. A; 1664 Rev. B ⁴² .	5520 B-2011 ³⁸ and 5520 F-2011 ³⁸
	Combustion	5310 B-2011	D7573-09	973.47, ³ p. 14. ²⁴
43. Organic nitrogen (as N), mg/L.	Heated persulfate or UV persulfate oxidation.	5310 C-2011, 5310 D-2011.	D4839-03	973.47, ³ p. 14. ²⁴
	Total Kjeldahl N (Parameter 31) minus ammonia N (Parameter 4).
44. Ortho-phosphate (as P), mg/L.	Ascorbic acid method:
	Automated	365.1, Rev. 2.0 (1993) ...	4500-P F-2011 or G-2011.	973.56, ³ I-4601-85. ²
	Manual single reagent	4500-P E-2011	D515-88 (A)	973.55. ³
	Manual two reagent	365.3 (Issued 1978) ¹
45. Osmium—Total, ⁴ mg/L.	Ion Chromatography	300.0, Rev. 2.1 (1993) and 300.1, Rev. 1.0 (1997).	4110 B-2011 or C-2011	D4327-03	993.30. ³
	CIE/UV	4140 B-2011	D6508-10	D6508, Rev. 2. ⁵⁴
	Digestion, ⁴ followed by any of the following:
	AA direct aspiration	3111 D-2011.
46. Oxygen, dissolved, mg/L.	AA furnace	252.2 (Issued 1978) ¹
	Winkler (Azide modification).	4500-O (B-F)-2011	D888-09 (A)	973.45B, ³ I-1575-78. ⁸
	Electrode	4500-O G-2011	D888-09 (B)	I-1576-78. ⁸
47. Palladium—Total, ⁴ mg/L.	Luminescence Based Sensor.	D888-09 (C)	See footnote. ⁶³ See footnote. ⁶⁴
	Digestion, ⁴ followed by any of the following:
	AA direct aspiration	3111 B-2011.
	AA furnace	253.2 (Issued 1978) ¹ .	3125 B-2011.
48. Phenols, mg/L	ICP/MS
	DCP	See footnote. ³⁴
	Manual distillation, ²⁶ followed by any of the following:	420.1 (Rev. 1978) ¹	5530 B-2010	D1783-01.
	Colorimetric (4AAP) manual.	420.1 (Rev. 1978) ¹	5530 D-2010 ²⁷	D1783-01 (A or B).
49. Phosphorus (elemental), mg/L.	Automated colorimetric (4AAP).	420.4 Rev. 1.0 (1993).
	Gas-liquid chromatography.	See footnote. ²⁸
50. Phosphorus—Total, mg/L.	Digestion, ²⁰ followed by any of the following:	4500-P B(5)-2011	973.55. ³
	Manual	365.3 (Issued 1978) ¹	4500-P E-2011	D515-88 (A).

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology ⁵⁸	EPA ⁵²	Standard methods	ASTM	USGS/AOAC/other
51. Platinum—Total ⁴ , mg/L.	Automated ascorbic acid reduction.	365.1 Rev. 2.0 (1993)	4500-P (F-H)—2011	973.56, ³ I-4600–85. ²
	ICP/AES ^{4,36}	200.7, Rev. 4.4 (1994) ...	3120 B–2011	I-4471–97. ⁵⁰
	Semi-automated block digester (TKP digestion).	365.4 (Issued 1974) ¹	D515–88 (B)	I-4610–91. ⁴⁸
	Digestion with persulfate, followed by Colorimetric.	NCASI TNTP W10900. ⁷⁷
	Digestion, ⁴ followed by any of the following:
52. Potassium—Total ⁴ , mg/L.	AA direct aspiration	3111 B–2011.
	AA furnace	255.2 (Issued 1978) ¹
	ICP/MS	3125 B–2011.	See footnote. ³⁴
	DCP
	Digestion, ⁴ followed by any of the following:
53. Residue—Total, mg/L.	AA direct aspiration	3111 B–2011	973.53, ³ I-3630–85. ²
	ICP/AES	200.7, Rev. 4.4 (1994) ...	3120 B–2011.
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14. ³
	Flame photometric	3500-K B–2011.
	Electrode	3500-K C–2011.
54. Residue—filterable, mg/L.	Ion Chromatography	D6919–09.
	Gravimetric, 103–105°	2540 B–2011	I-3750–85. ²
	Gravimetric, 180°	2540 C–2011	D5907–13	I-1750–85. ²
	Gravimetric, 103–105° post washing of residue.	2540 D–2011	D5907–13	I-3765–85. ²
	Volumetric, (Imhoff cone), or gravimetric.	2540 F–2011.
55. Residue—non-filterable (TSS), mg/L.	Gravimetric, 550°	160.4 (Issued 1971) ¹	2540-E–2011	I-3753–85. ²
56. Residue—settleable, mg/L.	Digestion, ⁴ followed by any of the following:
	AA direct aspiration, or	3111 B–2011.
	AA furnace	265.2 (Issued 1978) ¹
	ICP/MS	3125 B–2011.
	Digestion, ⁴ followed by any of the following:
57. Residue—Volatile, mg/L.	AA direct aspiration, or	3111 B–2011.
	AA furnace	267.2 ¹
	ICP/MS	3125 B–2011.
	Digestion, ⁴ followed by any of the following:
	AA direct aspiration, or	3111 B–2011.
58. Rhodium—Total ⁴ , mg/L.	AA furnace	3125 B–2011.
	ICP/MS
	Digestion, ⁴ followed by any of the following:
	AA direct aspiration, or	3111 B–2011.
	AA furnace	267.2 ¹
59. Ruthenium—Total ⁴ , mg/L.	ICP/MS	3125 B–2011.
	Digestion, ⁴ followed by any of the following:
	AA direct aspiration, or	3111 B–2011.
	AA furnace	267.2 ¹
	ICP/MS	3125 B–2011.
60. Selenium—Total ⁴ , mg/L.	Digestion, ⁴ followed by any of the following:
	AA furnace	3113 B–2010	D3859–08 (B)	I-4668–98. ⁴⁹
	STGFAA	200.9, Rev. 2.2 (1994).
	ICP/AES ³⁶	200.5, Rev. 4.2 (2003) ⁶⁸ ; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12.
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I-4020–05. ⁷⁰
61. Silica—Dissolved, ³⁷ mg/L.	AA gaseous hydride	3114 B–2011, or 3114 C–2011.	D3859–08 (A)	I-3667–85. ²
	0.45-micron filtration followed by any of the following:
	Colorimetric, Manual	4500-SiO ₂ C–2011	D859–10	I-1700–85. ²
	Automated (Molybdosilicate).	4500-SiO ₂ E–2011 or F–2011.	I-2700–85. ²
	ICP/AES	200.5, Rev. 4.2 (2003) ⁶⁸ ; 200.7, Rev. 4.4 (1994).	3120 B–2011	I-4471–97. ⁵⁰
62. Silver—Total, ^{4,31} mg/L.	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14. ³
	Digestion, ^{4,29} followed by any of the following:
	AA direct aspiration	3111 B–2011 or 3111 C–2011.	974.27, ³ p. 37, ⁹ I-3720–85. ²
	AA furnace	3113 B–2010	I-4724–89. ⁵¹
	STGFAA	200.9, Rev. 2.2 (1994).
63. Sodium—Total, ⁴ mg/L.	ICP/AES	200.5, Rev. 4.2 (2003) ⁶⁸ ; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I-4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14, ³ I-4471–97. ⁵⁰
	DCP	See footnote. ³⁴
	Digestion, ⁴ followed by any of the following:
	AA direct aspiration	3111 B–2011	973.54, ³ I-3735–85. ²
64. Specific conductance, micromhos/cm at 25 °C.	ICP/AES	200.5, Rev. 4.2 (2003) ⁶⁸ ; 200.7, Rev. 4.4 (1994).	3120 B–2011	I-4471–97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B–2011	D5673–10	993.14. ³
	DCP	See footnote. ³⁴
	Flame photometric	3500-Na B–2011.
	Ion Chromatography	D6919–09.
64. Specific conductance, micromhos/cm at 25 °C.	Wheatstone bridge	120.1 (Rev. 1982) ¹	2510 B–2011	D1125–95(99) (A)	973.40, ³ I-2781–85. ²

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology ⁵⁸	EPA ⁵²	Standard methods	ASTM	USGS/AOAC/other
65. Sulfate (as SO ₄), mg/L	Automated colorimetric ...	375.2, Rev. 2.0 (1993) ...	4500-SO ₄ ²⁻ F-2011 or G-2011.		
	Gravimetric	4500-SO ₄ ²⁻ C-2011 or D-2011.		925.54. ³
	Turbidimetric	4500-SO ₄ ²⁻ E-2011	D516-11.	
	Ion Chromatography	300.0, Rev. 2.1 (1993) and 300.1, Rev. 1.0 (1997).	4110 B-2011 or C-2011	D4327-03	993.30, ³ I-4020-05. ⁷⁰
66. Sulfide (as S), mg/L ..	CIE/UV	4140 B-2011	D6508-1010	D6508, Rev. 2. ⁵⁴
	Sample Pretreatment	4500-S ²⁻ B, C-2011.		
	Titrimetric (iodine)	4500-S ²⁻ F-2011		I-3840-85. ²
	Colorimetric (methylene blue).	4500-S ²⁻ D-2011.		
67. Sulfite (as SO ₃), mg/L	Ion Selective Electrode	4500-S ²⁻ G-2011	D4658-09.	
68. Surfactants, mg/L	Titrimetric (iodine-iodate)	4500-SO ₃ ²⁻ B-2011.		
	Colorimetric (methylene blue).	5540 C-2011	D2330-02.	
69. Temperature, °C	Thermometric	2550 B-2010		See footnote. ³²
70. Thallium—Total, ⁴ mg/L	Digestion, ⁴ followed by any of the following:				
	AA direct aspiration	3111 B-2011.		
	AA furnace	279.2 (Issued 1978) ¹	3113 B-2010.		
	STGFAA	200.9, Rev. 2.2 (1994).			
71. Tin—Total, ⁴ mg/L	ICP/AES	200.7, Rev. 4.4 (1994) ...	3120 B-2011	D1976-12.	
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B-2011	D5673-10	993.14, ³ I-4471-97. ⁵⁰
	Digestion, ⁴ followed by any of the following:				
	AA direct aspiration	3111 B-2011		I-3850-78. ⁸
72. Titanium—Total, ⁴ mg/L	AA furnace	3113 B-2010.		
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES	200.5, Rev. 4.2 (2003) ⁶⁸ , 200.7, Rev. 4.4 (1994).			
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B-2011	D5673-10	993.14. ³
73. Turbidity, NTU ⁵³	Digestion, ⁴ followed by any of the following:				
	AA direct aspiration	3111 D-2011.		
	AA furnace	283.2 (Issued 1978) ¹			
	ICP/AES	200.7, Rev. 4.4 (1994).			
74. Vanadium—Total, ⁴ mg/L	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B-2011	D5673-10	993.14. ³
	DCP			See footnote. ³⁴
	Nephelometric	180.1, Rev. 2.0 (1993) ...	2130 B-2011	D1889-00	I-3860-85. ² See footnote. ⁶⁵ See footnote. ⁶⁶ See footnote. ⁶⁷
75. Zinc—Total, ⁴ mg/L	Digestion, ⁴ followed by any of the following:				
	AA direct aspiration	3111 D-2011.		
	AA furnace	3113 B-2010	D3373-12.	
	ICP/AES	200.5, Rev. 4.2 (2003); ⁶⁸ 200.7, Rev. 4.4 (1994).	3120 B-2011	D1976-12	I-4471-97. ⁵⁰
76. Acid Mine Drainage ...	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B-2011	D5673-10	993.14, ³ I-4020-05. ⁷⁰
	DCP		D4190-08	See footnote. ³⁴
	Colorimetric (Gallic Acid)	3500-V B-2011.		
	Digestion, ⁴ followed by any of the following:				
77. Zinc—Total, ⁴ mg/L	AA direct aspiration ³⁶	3111 B-2011 or 3111 C-2011.	D1691-12 (A or B)	974.27, ³ p. 37, ⁹ I-3900-85. ²
	AA furnace	289.2 (Issued 1978) ¹			
	ICP/AES ³⁶	200.5, Rev. 4.2 (2003) ⁶⁸ , 200.7, Rev. 4.4 (1994).	3120 B-2011	D1976-12	I-4471-97. ⁵⁰
	ICP/MS	200.8, Rev. 5.4 (1994) ...	3125 B-2011	D5673-10	993.14, ³ I-4020-05. ⁷⁰
78. Acid Mine Drainage ...	DCP ³⁶		D4190-08	See footnote. ³⁴
	Colorimetric (Zincon)	3500 Zn B-2011		See footnote. ³³
79. Acid Mine Drainage	1627 ⁶⁹ .			

Table IB Notes:¹ Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020. Revised March 1983 and 1979, where applicable. U.S. EPA.² Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water-Resource Investigations of the U.S. Geological Survey, Book 5, Chapter A1., unless otherwise stated. 1989. USGS.³ Official Methods of Analysis of the Association of Official Analytical Chemists, Methods Manual, Sixteenth Edition, 4th Revision, 1998. AOAC International.⁴ For the determination of total metals (which are equivalent to total recoverable metals) the sample is not filtered before processing. A digestion procedure is required to solubilize analytes in suspended material and to break down organic-metal complexes (to convert the analyte to a detectable form for colorimetric analysis). For non-platform graphite furnace atomic absorption determinations, a digestion using nitric acid (as specified in Section 4.1.3 of Methods for the Chemical Analysis of Water and Wastes) is required prior to analysis. The procedure used should subject the sample to gentle, acid refluxing and at no time should the sample be taken to dryness. For direct aspiration flame atomic absorption determinations (FLAA) a combination acid (nitric and hydrochloric acids) digestion is preferred prior to analysis. The approved total recoverable digestion is described as Method 200.2 in Supplement I of "Methods for the Determination of Metals in Environmental Samples" EPA/600R-94/111, May, 1994, and is reproduced in EPA Methods 200.7, 200.8, and 200.9 from the same Supplement. However, when using the gaseous hydride technique or for the determination of certain elements such as antimony, arsenic, selenium, silver, and tin by non-EPA graphite furnace atomic absorption methods, mercury by cold vapor atomic absorption, the noble metals and titanium by FLAA, a specific or modified sample digestion procedure may be required and in all cases the referenced method write-up should be consulted for specific instruction and/or cautions. For analyses using inductively coupled plasma-atomic emission spectrometry (ICP-AES), the direct current plasma (DCP) technique or EPA spectrochemical techniques (platform furnace AA, ICP-AES, and ICP-MS) use EPA Method 200.2 or an approved alternate procedure (e.g., CEM microwave digestion, which may be used with certain analytes as indicated in Table IB); the total recoverable digestion procedures in EPA Methods 200.7, 200.8, and 200.9 may be used for those respective methods. Regardless of the digestion procedure, the results of the analysis after digestion procedure are reported as "total" metals.⁵ Copper sulfate or other catalysts that have been found suitable may be used in place of mercuric sulfate.

⁶ Manual distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary. However, manual distillation will be required to resolve any controversies. In general, the analytical method should be consulted regarding the need for distillation. If the method is not clear, the laboratory may compare a minimum of 9 different sample matrices to evaluate the need for distillation. For each matrix, a matrix spike and matrix spike duplicate are analyzed both with and without the distillation step. (A total of 36 samples, assuming 9 matrices). If results are comparable, the laboratory may dispense with the distillation step for future analysis. Comparable is defined as <20% RPD for all tested matrices). Alternatively the two populations of spike recovery percentages may be compared using a recognized statistical test.

⁷ Industrial Method Number 379–75 WE Ammonia, Automated Electrode Method, Technicon Auto Analyzer II. February 19, 1976. Bran & Luebbe Analyzing Technologies Inc.

⁸ The approved method is that cited in Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A1. 1979. USGS.

⁹ American National Standard on Photographic Processing Effluents. April 2, 1975. American National Standards Institute.

¹⁰ In-Situ Method 1003–8–2009, Biochemical Oxygen Demand (BOD) Measurement by Optical Probe. 2009. In-Situ Incorporated.

¹¹ The use of normal and differential pulse voltage ramps to increase sensitivity and resolution is acceptable.

¹² Carbonaceous biochemical oxygen demand (CBOD₅) must not be confused with the traditional BOD₅ test method which measures “total 5-day BOD.” The addition of the nitrification inhibitor is not a procedural option, but must be included to report the CBOD₅ parameter. A discharger whose permit requires reporting the traditional BOD₅ may not use a nitrification inhibitor in the procedure for reporting the results. Only when a discharger’s permit specifically states CBOD₅ is required can the permittee report data using a nitrification inhibitor.

¹³ OIC Chemical Oxygen Demand Method. 1978. Oceanography International Corporation.

¹⁴ Method 8000, Chemical Oxygen Demand, Hach Handbook of Water Analysis, 1979. Hach Company.

¹⁵ The back titration method will be used to resolve controversy.

¹⁶ Orion Research Instruction Manual, Residual Chlorine Electrode Model 97–70. 1977. Orion Research Incorporated. The calibration graph for the Orion residual chlorine method must be derived using a reagent blank and three standard solutions, containing 0.2, 1.0, and 5.0 mL 0.00281 N potassium iodate/100 mL solution, respectively.

¹⁷ Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, EPA–821–R–05–001. Revision 2.0, February 2005. US EPA.

¹⁸ National Council of the Paper Industry for Air and Stream Improvement (NCASI) Technical Bulletin 253 (1971) and Technical Bulletin 803, May 2000.

¹⁹ Method 8506, Bicinchoninate Method for Copper, Hach Handbook of Water Analysis. 1979. Hach Company.

²⁰ When using a method with block digestion, this treatment is not required.

²¹ Industrial Method Number 378–75WA, Hydrogen ion (pH) Automated Electrode Method, Bran & Luebbe (Technicon) Autoanalyzer II. October 1976. Bran & Luebbe Analyzing Technologies.

²² Method 8008, 1,10-Phenanthroline Method using FerroVer Iron Reagent for Water. 1980. Hach Company.

²³ Method 8034, Periodate Oxidation Method for Manganese, Hach Handbook of Wastewater Analysis. 1979. Hach Company.

²⁴ Methods for Analysis of Organic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A3, (1972 Revised 1987). 1987. USGS.

²⁵ Method 8507, Nitrogen, Nitrite-Low Range, Diazotization Method for Water and Wastewater. 1979. Hach Company.

²⁶ Just prior to distillation, adjust the sulfuric-acid-preserved sample to pH 4 with 1 + 9 NaOH.

²⁷ The colorimetric reaction must be conducted at a pH of 10.0 ± 0.2.

²⁸ Addison, R.F., and R.G. Ackman. 1970. Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography, *Journal of Chromatography*, 47(3):421–426.

²⁹ Approved methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/L and above are inadequate where silver exists as an inorganic halide. Silver halides such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to pH of 12. Therefore, for levels of silver above 1 mg/L, 20 mL of sample should be diluted to 100 mL by adding 40 mL each of 2 M Na₂S₂O₃ and NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/L the approved method is satisfactory.

³⁰ The use of EDTA decreases method sensitivity. Analysts may omit EDTA or replace with another suitable complexing reagent provided that all method specified quality control acceptance criteria are met.

³¹ For samples known or suspected to contain high levels of silver (e.g., in excess of 4 mg/L), cyanogen iodide should be used to keep the silver in solution for analysis. Prepare a cyanogen iodide solution by adding 4.0 mL of concentrated NH₄OH, 6.5 g of KCN, and 5.0 mL of a 1.0 N solution of I₂ to 50 mL of reagent water in a volumetric flask and dilute to 100.0 mL. After digestion of the sample, adjust the pH of the digestate to >7 to prevent the formation of HCN under acidic conditions. Add 1 mL of the cyanogen iodide solution to the sample digestate and adjust the volume to 100 mL with reagent water (NOT acid). If cyanogen iodide is added to sample digestates, then silver standards must be prepared that contain cyanogen iodide as well. Prepare working standards by diluting a small volume of a silver stock solution with water and adjusting the pH>7 with NH₄OH. Add 1 mL of the cyanogen iodide solution and let stand 1 hour. Transfer to a 100-mL volumetric flask and dilute to volume with water.

³² “Water Temperature-Influential Factors, Field Measurement and Data Presentation,” Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 1, Chapter D1. 1975. USGS.

³³ Method 8009, Zincon Method for Zinc, Hach Handbook of Water Analysis, 1979. Hach Company.

³⁴ Method AES0029, Direct Current Plasma (DCP) Optical Emission Spectrometric Method for Trace Elemental Analysis of Water and Wastes. 1986-Revised 1991. Thermo Jarrell Ash Corporation.

³⁵ In-Situ Method 1004–8–2009, Carbonaceous Biochemical Oxygen Demand (CBOD) Measurement by Optical Probe. 2009. In-Situ Incorporated.

³⁶ Microwave-assisted digestion may be employed for this metal, when analyzed by this methodology. Closed Vessel Microwave Digestion of Wastewater Samples for Determination of Metals. April 16, 1992. CEM Corporation.

³⁷ When determining boron and silica, only plastic, PTFE, or quartz laboratory ware may be used from start until completion of analysis.

³⁸ Only use n-hexane (n-Hexane—85% minimum purity, 99.0% min. saturated C6 isomers, residue less than 1 mg/L) extraction solvent when determining Oil and Grease parameters—Hexane Extractable Material (HEM), or Silica Gel Treated HEM (analogous to EPA Methods 1664 Rev. A and 1664 Rev. B). Use of other extraction solvents is prohibited.

³⁹ Method PAI–DK01, Nitrogen, Total Kjeldahl, Block Digestion, Steam Distillation, Titrimetric Detection. Revised December 22, 1994. OI Analytical.

⁴⁰ Method PAI–DK02, Nitrogen, Total Kjeldahl, Block Digestion, Steam Distillation, Colorimetric Detection. Revised December 22, 1994. OI Analytical.

⁴¹ Method PAI–DK03, Nitrogen, Total Kjeldahl, Block Digestion, Automated FIA Gas Diffusion. Revised December 22, 1994. OI Analytical.

⁴² Method 1664 Rev. B is the revised version of EPA Method 1664 Rev. A. U.S. EPA. February 1999, Revision A. Method 1664, n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT–HEM; Non-polar Material) by Extraction and Gravimetry. EPA–821–R–98–002. U.S. EPA. February 2010, Revision B. Method 1664, n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT–HEM; Non-polar Material) by Extraction and Gravimetry. EPA–821–R–10–001.

⁴³ Method 1631, Revision E, Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, EPA–821–R–02–019. Revision E. August 2002. U.S. EPA. The application of clean techniques described in EPA’s Method 1669: *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*, EPA–821–R–96–011, are recommended to preclude contamination at low-level, trace metal determinations.

⁴⁴ Method OIA–1677–09, Available Cyanide by Ligand Exchange and Flow Injection Analysis (FIA). 2010. OI Analytical.

⁴⁵ Open File Report 00–170, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Ammonium Plus Organic Nitrogen by a Kjeldahl Digestion Method and an Automated Photometric Finish that Includes Digest Cleanup by Gas Diffusion. 2000. USGS.

⁴⁶ Open File Report 93–449, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Chromium in Water by Graphite Furnace Atomic Absorption Spectrophotometry. 1993. USGS.

⁴⁷ Open File Report 97–198, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Molybdenum by Graphite Furnace Atomic Absorption Spectrophotometry. 1997. USGS.

⁴⁸ Open File Report 92–146, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Total Phosphorus by Kjeldahl Digestion Method and an Automated Colorimetric Finish That Includes Dialysis. 1992. USGS.

⁴⁹ Open File Report 98–639, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Arsenic and Selenium in Water and Sediment by Graphite Furnace-Atomic Absorption Spectrometry. 1999. USGS.

⁵⁰ Open File Report 98–165, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Elements in Whole-water Digests Using Inductively Coupled Plasma-Optical Emission Spectrometry and Inductively Coupled Plasma-Mass Spectrometry. 1998. USGS.

⁵¹ Open File Report 93–125, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments. 1993. USGS.

⁵² Unless otherwise indicated, all EPA methods, excluding EPA Method 300.1, are published in U.S. EPA. May 1994. Methods for the Determination of Metals in Environmental Samples, Supplement I, EPA/600/R–94/111; or U.S. EPA. August 1993. Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R–93/100. EPA Method 300.1 is US EPA. Revision 1.0, 1997, including errata cover sheet April 27, 1999. Determination of Inorganic Ions in Drinking Water by Ion Chromatography.

⁵³ Styrene divinyl benzene beads (e.g., AMCO–AEPA–1 or equivalent) and stabilized formazin (e.g., Hach StablCal™ or equivalent) are acceptable substitutes for formazin.

⁵⁴ Method D6508–10, Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte. 2010. ASTM.

⁵⁵ Kelada-01, Kelada Automated Test Methods for Total Cyanide, Acid Dissociable Cyanide, and Thiocyanate, EPA 821-B-01-009, Revision 1.2, August 2001. US EPA. Note: A 450-W UV lamp may be used in this method instead of the 550-W lamp specified if it provides performance within the quality control (QC) acceptance criteria of the method in a given instrument. Similarly, modified flow cell configurations and flow conditions may be used in the method, provided that the QC acceptance criteria are met.

⁵⁶ QuikChem Method 10-204-00-1-X, Digestion and Distillation of Total Cyanide in Drinking and Wastewaters using MICRO DIST and Determination of Cyanide by Flow Injection Analysis. Revision 2.2, March 2005. Lachat Instruments.

⁵⁷ When using sulfide removal test procedures described in EPA Method 335.4-1, reconstitute particulate that is filtered with the sample prior to distillation.

⁵⁸ Unless otherwise stated, if the language of this table specifies a sample digestion and/or distillation "followed by" analysis with a method, approved digestion and/or distillation are required prior to analysis.

⁵⁹ Samples analyzed for available cyanide using OI Analytical method OIA-1677-09 or ASTM method D6888-09 that contain particulate matter may be filtered only after the ligand exchange reagents have been added to the samples, because the ligand exchange process converts complexes containing available cyanide to free cyanide, which is not removed by filtration. Analysts are further cautioned to limit the time between the addition of the ligand exchange reagents and sample filtration to no more than 30 minutes to preclude settling of materials in samples.

⁶⁰ Analysts should be aware that pH optima and chromophore absorption maxima might differ when phenol is replaced by a substituted phenol as the color reagent in Berthelot Reaction ("phenol-hypochlorite reaction") colorimetric ammonium determination methods. For example when phenol is used as the color reagent, pH optimum and wavelength of maximum absorbance are about 11.5 and 635 nm, respectively—see, Patton, C.J. and S.R. Crouch. March 1977. Anal. Chem. 49:464-469. These reaction parameters increase to pH > 12.6 and 665 nm when salicylate is used as the color reagent—see, Krom, M.D. April 1980. The Analyst 105:305-316.

⁶¹ If atomic absorption or ICP instrumentation is not available, the aluminum colorimetric method detailed in the 19th Edition of *Standard Methods* may be used. This method has poorer precision and bias than the methods of choice.

⁶² Easy (1-Reagent) Nitrate Method, Revision November 12, 2011. Craig Chinchilla.

⁶³ Hach Method 10360, Luminescence Measurement of Dissolved Oxygen in Water and Wastewater and for Use in the Determination of BOD₅ and cBOD₅. Revision 1.2, October 2011. Hach Company. This method may be used to measure dissolved oxygen when performing the methods approved in Table IB for measurement of biochemical oxygen demand (BOD) and carbonaceous biochemical oxygen demand (CBOD).

⁶⁴ In-Situ Method 1002-8-2009, Dissolved Oxygen (DO) Measurement by Optical Probe. 2009. In-Situ Incorporated.

⁶⁵ Mitchell Method M5331, Determination of Turbidity by Nephelometry. Revision 1.0, July 31, 2008. Leck Mitchell.

⁶⁶ Mitchell Method M5271, Determination of Turbidity by Nephelometry. Revision 1.0, July 31, 2008. Leck Mitchell.

⁶⁷ Orion Method AQ4500, Determination of Turbidity by Nephelometry. Revision 5, March 12, 2009. Thermo Scientific.

⁶⁸ EPA Method 200.5, Determination of Trace Elements in Drinking Water by Axially Viewed Inductively Coupled Plasma-Atomic Emission Spectrometry, EPA/600/R-06/115. Revision 4.2. October 2003. US EPA.

⁶⁹ Method 1627, Kinetic Test Method for the Prediction of Mine Drainage Quality, EPA-821-R-09-002. December 2011. US EPA.

⁷⁰ Techniques and Methods Book 5-B1, Determination of Elements in Natural-Water, Biota, Sediment and Soil Samples Using Collision/Reaction Cell Inductively Coupled Plasma-Mass Spectrometry, Chapter 1, Section B, Methods of the National Water Quality Laboratory, Book 5, Laboratory Analysis, 2006. USGS.

⁷¹ Water-Resources Investigations Report 01-4132, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Organic Plus Inorganic Mercury in Filtered and Unfiltered Natural Water with Cold Vapor-Atomic Fluorescence Spectrometry, 2001. USGS.

⁷² USGS Techniques and Methods 5-B8, Chapter 8, Section B, Methods of the National Water Quality Laboratory Book 5, Laboratory Analysis, 2011 USGS.

⁷³ NECi Method N07-0003, "Nitrate Reductase Nitrate-Nitrogen Analysis," Revision 9.0, March 2014, The Nitrate Elimination Co., Inc.

⁷⁴ Timberline Instruments, LLC Method Ammonia-001, "Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Conductivity Cell Analysis," June 2011, Timberline Instruments, LLC.

⁷⁵ Hach Company Method 10206, "Spectrophotometric Measurement of Nitrate in Water and Wastewater," Revision 2.1, January 2013, Hach Company.

⁷⁶ Hach Company Method 10242, "Simplified Spectrophotometric Measurement of Total Kjeldahl Nitrogen in Water and Wastewater," Revision 1.1, January 2013, Hach Company.

⁷⁷ National Council for Air and Stream Improvement (NCASI) Method TNTP-W10900, "Total (Kjeldahl) Nitrogen and Total Phosphorus in Pulp and Paper Biologically Treated Effluent by Alkaline Persulfate Digestion," June 2011, National Council for Air and Stream Improvement, Inc.

⁷⁸ The pH adjusted sample is to be adjusted to 7.6 for NPDES reporting purposes.

TABLE IC—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS

Parameter ¹	Method	EPA ^{2,7}	Standard methods	ASTM	Other
1. Acenaphthene	GC	610
	GC/MS	625.1, 1625B	6410 B-2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B-2005	D4657-92 (98)
2. Acenaphthylene	GC	610
	GC/MS	625.1, 1625B	6410 B-2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B-2005	D4657-92 (98)
3. Acrolein	GC	603
	GC/MS	624.1, ⁴ 1624B
4. Acrylonitrile	GC	603
	GC/MS	624.1, ⁴ 1624B
5. Anthracene	GC	610
	GC/MS	625.1, 1625B	6410 B-2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B-2005	D4657-92 (98)
6. Benzene	GC	602	6200 C-2011
	GC/MS	624.1, 1624B	6200 B-2011
7. Benzidine	Spectro-photometric	See footnote, ³ p.1.
	GC/MS	625.1 ⁵ , 1625B	6410 B-2000
	HPLC	605
8. Benzo(a)anthracene	GC	610
	GC/MS	625.1, 1625B	6410 B-2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B-2005	D4657-92 (98)
9. Benzo(a)pyrene	GC	610
	GC/MS	625.1, 1625B	6410 B-2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B-2005	D4657-92 (98)
10. Benzo(b)fluoranthene	GC	610
	GC/MS	625.1, 1625B	6410 B-2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B-2005	D4657-92 (98)
11. Benzo(g,h,i)perylene	GC	610
	GC/MS	625.1, 1625B	6410 B-2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B-2005	D4657-92 (98)
12. Benzo(k)fluoranthene	GC	610
	GC/MS	625.1, 1625B	6410 B-2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B-2005	D4657-92 (98)
13. Benzyl chloride	GC	See footnote, ³ p. 130.
	GC/MS	See footnote, ⁶ p. S102.
14. Butyl benzyl phthalate	GC	606
	GC/MS	625.1, 1625B	6410 B-2000	See footnote, ⁹ p. 27.
15. bis(2-Chloroethoxy) methane ..	GC	611
	GC/MS	625.1, 1625B	6410 B-2000	See footnote, ⁹ p. 27.
16. bis(2-Chloroethyl) ether	GC	611
	GC/MS	625.1, 1625B	6410 B-2000	See footnote, ⁹ p. 27.
17. bis(2-Ethylhexyl) phthalate	GC	606

TABLE IC—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS—Continued

Parameter ¹	Method	EPA ^{2,7}	Standard methods	ASTM	Other
18. Bromodichloromethane	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
19. Bromoform	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
20. Bromomethane	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
21. 4-Bromophenyl phenyl ether ...	GC	611	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
22. Carbon tetrachloride	GC	601	6200 C–2011	See footnote, ³ p. 130.
	GC/MS	624.1, 1624B	6200 B–2011	
23. 4-Chloro-3-methyl phenol	GC	604	6420 B–2000	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
24. Chlorobenzene	GC	601, 602	6200 C–2011	See footnote, ³ p. 130.
	GC/MS	624.1, 1624B	6200 B–2011	
25. Chloroethane	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
26. 2-Chloroethylvinyl ether	GC	601	
	GC/MS	624.1, 1624B	
27. Chloroform	GC	601	6200 C–2011	See footnote, ³ p. 130.
	GC/MS	624.1, 1624B	6200 B–2011	
28. Chloromethane	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
29. 2-Chloronaphthalene	GC	612	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
30. 2-Chlorophenol	GC	604	6420 B–2000	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
31. 4-Chlorophenyl phenyl ether ...	GC	611	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
32. Chrysene	GC	610	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
33. Dibenzo(a,h)anthracene	GC	610	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
34. Dibromochloromethane	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
35. 1,2-Dichlorobenzene	GC	601, 602	6200 C–2011	
	GC/MS	624.1, 1625B	6200 B–2011	See footnote, ⁹ p. 27.
36. 1,3-Dichlorobenzene	GC	601, 602	6200 C–2011	
	GC/MS	624.1, 1625B	6200 B–2011	See footnote, ⁹ p. 27.
37. 1,4-Dichlorobenzene	GC	601, 602	6200 C–2011	
	GC/MS	624.1, 1625B	6200 B–2011	See footnote, ⁹ p. 27.
38. 3,3'-Dichlorobenzidine	GC/MS	625.1, 1625B	6410 B–2000	
	HPLC	605	
39. Dichlorodifluoromethane	GC	601	
	GC/MS	6200 C–2011	
40. 1,1-Dichloroethane	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
41. 1,2-Dichloroethane	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
42. 1,1-Dichloroethene	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
43. trans-1,2-Dichloroethene	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
44. 2,4-Dichlorophenol	GC	604	6420 B–2000	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
45. 1,2-Dichloropropane	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
46. cis-1,3-Dichloropropene	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
47. trans-1,3-Dichloropropene	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
48. Diethyl phthalate	GC	606	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
49. 2,4-Dimethylphenol	GC	604	6420 B–2000	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
50. Dimethyl phthalate	GC	606	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
51. Di-n-butyl phthalate	GC	606	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
52. Di-n-octyl phthalate	GC	606	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
53. 2, 4-Dinitrophenol	GC	604	6420 B–2000	See footnote, ⁹ p. 27.
	GC/MS	625.1, 1625B	6410 B–2000	
54. 2,4-Dinitrotoluene	GC	609	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
55. 2,6-Dinitrotoluene	GC	609	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
56. Epichlorohydrin	GC	See footnote, ³ p. 130.
	GC/MS	See footnote, ⁶ p. S102.

TABLE IC—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS—Continued

Parameter ¹	Method	EPA ^{2,7}	Standard methods	ASTM	Other
57. Ethylbenzene	GC	602	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
58. Fluoranthene	GC	610	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
59. Fluorene	GC	610	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
60. 1,2,3,4,6,7,8-Heptachloro- dibenzofuran.	GC/MS	1613B	
61. 1,2,3,4,7,8,9-Heptachloro- dibenzofuran.	GC/MS	1613B	
62. 1,2,3,4,6,7,8- Heptachloro- dibenzo- <i>p</i> -dioxin.	GC/MS	1613B	
63. Hexachlorobenzene	GC	612	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
64. Hexachlorobutadiene	GC	612	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
65. Hexachlorocyclopentadiene	GC	612	
	GC/MS	625.1, ⁵ 1625B	6410 B–2000	See footnote, ⁹ p. 27.
	GC/MS	1613B	
66. 1,2,3,4,7,8-Hexachloro- dibenzofuran.	GC/MS	1613B	
67. 1,2,3,6,7,8-Hexachloro- dibenzofuran.	GC/MS	1613B	
68. 1,2,3,7,8,9-Hexachloro- dibenzofuran.	GC/MS	1613B	
69. 2,3,4,6,7,8-Hexachloro- dibenzofuran.	GC/MS	1613B	
70. 1,2,3,4,7,8-Hexachloro- dibenzo- <i>p</i> -dioxin.	GC/MS	1613B	
71. 1,2,3,6,7,8-Hexachloro- dibenzo- <i>p</i> -dioxin.	GC/MS	1613B	
72. 1,2,3,7,8,9-Hexachloro- dibenzo- <i>p</i> -dioxin.	GC/MS	1613B	
73. Hexachloroethane	GC	612	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
74. Indeno(1,2,3- <i>c,d</i>) pyrene	GC	610	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
75. Isophorone	GC	609	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
76. Methylene chloride	GC	601	6200 C–2011	See footnote, ³ p. 130.
	GC/MS	624.1, 1624B	6200 B–2011	
77. 2-Methyl-4,6-dinitrophenol	GC	604	6420 B–2000	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
78. Naphthalene	GC	610	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B–2005	
79. Nitrobenzene	GC	609	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
	HPLC	D4657–92 (98)	
80. 2-Nitrophenol	GC	604	6420 B–2000	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
81. 4-Nitrophenol	GC	604	6420 B–2000	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
82. N-Nitrosodimethylamine	GC	607	
	GC/MS	625.1, ⁵ 1625B	6410 B–2000	See footnote, ⁹ p. 27.
83. N-Nitrosodi- <i>n</i> -propylamine	GC	607	
	GC/MS	625.1, ⁵ 1625B	6410 B–2000	See footnote, ⁹ p. 27.
84. N-Nitrosodiphenylamine	GC	607	
	GC/MS	625.1, ⁵ 1625B	6410 B–2000	See footnote, ⁹ p. 27.
85. Octachlorodibenzofuran	GC/MS	1613B ¹⁰	
86. Octachlorodibenzo- <i>p</i> -dioxin	GC/MS	1613B ¹⁰	
87. 2,2'-oxybis(1-chloropropane) ¹² [also known as bis(2-Chloro-1- methylethyl) ether].	GC	611	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
88. PCB–1016	GC	608.3	See footnote, ³ p. 43; See footnote. ⁸
	GC/MS	625.1	6410 B–2000	
89. PCB–1221	GC	608.3	See footnote, ³ p. 43; See footnote. ⁸
	GC/MS	625.1	6410 B–2000	
90. PCB–1232	GC	608.3	See footnote, ³ p. 43; See footnote. ⁸
	GC/MS	625.1	6410 B–2000	
91. PCB–1242	GC	608.3	See footnote, ³ p. 43; See footnote. ⁸
	GC/MS	625.1	6410 B–2000	
92. PCB–1248	GC	608.3	See footnote, ³ p. 43; See footnote. ⁸

TABLE IC—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS—Continued

Parameter ¹	Method	EPA ^{2,7}	Standard methods	ASTM	Other
93. PCB–1254	GC/MS	625.1	6410 B–2000	See footnote, ³ p. 43; See footnote. ⁸
	GC	608.3	
94. PCB–1260	GC/MS	625.1	6410 B–2000	See footnote, ³ p. 43; See footnote. ⁸
	GC	608.3	
95. 1,2,3,7,8-Pentachloro-dibenzofuran.	GC/MS	625.1	6410 B–2000	
96. 2,3,4,7,8-Pentachloro-dibenzofuran.	GC/MS	1613B	
97. 1,2,3,7,8-Pentachloro-dibenzo- <i>p</i> -dioxin.	GC/MS	1613B	
98. Pentachlorophenol	GC	604	6420 B–2000	See footnote, ³ p. 140.
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
99. Phenanthrene	GC	610	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
100. Phenol	GC	604	6420 B–2000	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
101. Pyrene	GC	610	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
102. 2,3,7,8-Tetrachloro-dibenzofuran.	GC/MS	1613B ¹⁰	
103. 2,3,7,8-Tetrachloro-dibenzo- <i>p</i> -dioxin.	GC/MS	613, 625.1, ^{5a} 1613B.	
104. 1,1,2,2-Tetrachloroethane	GC	601	6200 C–2011	See footnote, ³ p. 130.
	GC/MS	624.1, 1624B	6200 B–2011	
105. Tetrachloroethene	GC	601	6200 C–2011	See footnote, ³ p. 130.
	GC/MS	624.1, 1624B	6200 B–2011	
106. Toluene	GC	602	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
107. 1,2,4-Trichlorobenzene	GC	612	See footnote, ³ p. 130.
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
108. 1,1,1-Trichloroethane	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
109. 1,1,2-Trichloroethane	GC	601	6200 C–2011	See footnote, ³ p. 130.
	GC/MS	624.1, 1624B	6200 B–2011	
110. Trichloroethene	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
111. Trichlorofluoromethane	GC	601	6200 C–2011	
	GC/MS	624.1	6200 B–2011	
112. 2,4,6-Trichlorophenol	GC	604	6420 B–2000	
	GC/MS	625.1, 1625B	6410 B–2000	See footnote, ⁹ p. 27.
113. Vinyl chloride	GC	601	6200 C–2011	
	GC/MS	624.1, 1624B	6200 B–2011	
114. Nonylphenol	GC/MS	D7065–11	
115. Bisphenol A (BPA)	GC/MS	D7065–11	
116. <i>p</i> -tert-Octylphenol (OP)	GC/MS	D7065–11	
117. Nonylphenol Monoethoxylate (NP1EO)	GC/MS	D7065–11	
118. Nonylphenol Diethoxylate (NP2EO)	GC/MS	D7065–11	
119. Adsorbable Organic Halides (AOX)	Adsorption and Coulometric Titration.	1650 ¹¹	
120. Chlorinated Phenolics	In Situ Acetylation and GC/MS.	1653 ¹¹	

Table IC notes:

¹ All parameters are expressed in micrograms per liter (µg/L) except for Method 1613B, in which the parameters are expressed in picograms per liter (pg/L).² The full text of Methods 601–613, 1613B, 1624B, and 1625B are provided at appendix A, Test Procedures for Analysis of Organic Pollutants. The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at appendix B of this part, Definition and Procedure for the Determination of the Method Detection Limit. These methods are available at: <https://www.epa.gov/cwa-methods> as individual PDF files.³ Methods for Benzidine: Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater. September 1978. U.S. EPA.⁴ Method 624.1 may be used for quantitative determination of acrolein and acrylonitrile, provided that the laboratory has documentation to substantiate the ability to detect and quantify these analytes at levels necessary to comply with any associated regulations. In addition, the use of sample introduction techniques other than simple purge-and-trap may be required. QC acceptance criteria from Method 603 should be used when analyzing samples for acrolein and acrylonitrile in the absence of such criteria in Method 624.1.⁵ Method 625.1 may be extended to include benzidine, hexachlorocyclopentadiene, N-nitrosodimethylamine, N-nitrosodi-n-propylamine, and N-nitrosodiphenylamine. However, when they are known to be present, Methods 605, 607, and 612, or Method 1625B, are preferred methods for these compounds.^{5a} Method 625.1 screening only.⁶ Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency, Supplement to the 15th Edition of *Standard Methods for the Examination of Water and Wastewater*. 1981. American Public Health Association (APHA).⁷ Each analyst must make an initial, one-time demonstration of their ability to generate acceptable precision and accuracy with Methods 601–603, 1624B, and 1625B in accordance with procedures each in Section 8.2 of each of these Methods. Additionally, each laboratory, on an on-going basis must spike and analyze 10% (5% for Methods 624.1 and 625.1 and 100% for methods 1624B and 1625B) of all samples to monitor and evaluate laboratory data quality in accordance with Sections 8.3 and 8.4 of these methods. When the recovery of any parameter falls outside the quality control (QC) acceptance criteria in the pertinent method, analytical results for that parameter in the unspiked sample are suspect. The results should be reported but cannot be used to demonstrate regulatory compliance. If the method does not contain QC acceptance criteria, control limits of \pm three standard deviations around the mean of a minimum of five replicate measurements must be used. These quality control requirements also apply to the Standard Methods, ASTM Methods, and other methods cited.⁸ Organochlorine Pesticides and PCBs in Wastewater Using Empore™ Disk. Revised October 28, 1994. 3M Corporation.⁹ Method O–3116–87 is in Open File Report 93–125, Methods of Analysis by U.S. Geological Survey National Water Quality Laboratory—Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments. 1993. USGS.

¹⁰ Analysts may use Fluid Management Systems, Inc. Power-Prep system in place of manual cleanup provided the analyst meets the requirements of Method 1613B (as specified in Section 9 of the method) and permitting authorities. Method 1613, Revision B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. Revision B, 1994. U.S. EPA. The full text of this method is provided in appendix A to this part and at <https://www.epa.gov/cwa-methods/ap-proved-cwa-methods-organic-compounds>.

¹¹ Method 1650, Adsorbable Organic Halides by Adsorption and Coulometric Titration. Revision C, 1997 U.S. EPA. Method 1653, Chlorinated Phenolics in Wastewater by In Situ Acetylation and GCMS. Revision A, 1997 U.S. EPA. The full text for both of these methods is provided at appendix A in part 430 of this chapter, The Pulp, Paper, and Paperboard Point Source Category.

¹² The compound was formerly inaccurately labeled as 2,2'-oxybis(2-chloropropane) and bis(2-chloroisopropyl) ether. Some versions of Methods 611, and 1625 inaccurately list the analyte as "bis(2-chloroisopropyl)ether," but use the correct CAS number of 108-60-1.

TABLE ID—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES ¹

Parameter	Method	EPA ^{2 7 10}	Standard methods	ASTM	Other
1. Aldrin	GC	617, 608.3	6630 B-2007 & C-2007	D3086-90, D5812-96 (02).	See footnote, ³ p. 7; See footnote, ⁴ O-3104-83; See footnote, ⁸ 3M0222.
2. Ametryn	GC/MS	625.1	6410 B-2000.		See footnote, ³ p. 83; See footnote, ⁹ O-3106-93; See footnote, ⁶ p. S68.
	GC	507, 619			See footnote, ¹⁴ O-1121-91.
3. Aminocarb	GC/MS	525.2, 625.1			See footnote, ³ p. 94; See footnote, ⁶ p. S60.
	TLC				
4. Atraton	HPLC	632.			See footnote, ³ p. 83; See footnote, ⁶ p. S68.
	GC	619			
5. Atrazine	GC/MS	625.1.			See footnote, ³ p. 83; See footnote, ⁶ p. S68; See footnote, ⁹ O-3106-93.
	GC	507, 619, 608.3			See footnote, ¹² O-2060-01.
6. Azinphos methyl	HPLC/MS				See footnote, ¹¹ O-1126-95.
	GC/MS	525.1, 525.2, 625.1			See footnote, ³ p. 25; See footnote, ⁶ p. S51.
	GC	614, 622, 1657			See footnote, ¹¹ O-1126-95.
7. Barban	GC/MS	625.1			See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	TLC				
8. α -BHC	HPLC	632.	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7; See footnote, ⁸ 3M0222.
	GC/MS	625.1.			See footnote, ¹¹ O-1126-95.
9. β -BHC	GC	617, 608.3	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ⁸ 3M0222.
	GC/MS	625.1	6410 B-2000.		
10. δ -BHC	GC	617, 608.3	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ⁸ 3M0222.
11. γ -BHC (Lindane)	GC/MS	625.1	6410 B-2000.		See footnote, ³ p. 7; See footnote, ⁴ O-3104-83; See footnote, ⁸ 3M0222.
	GC	617, 608.3	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ¹¹ O-1126-95.
12. Captan	GC/MS	625.1 ⁵	6410 B-2000		See footnote, ³ p. 7.
	GC	617, 608.3	6630 B-2007	D3086-90, D5812-96(02).	
13. Carbaryl	TLC				See footnote, ³ p. 94, See footnote, ⁶ p. S60.
	HPLC	531.1, 632.			See footnote, ¹² O-2060-01.
	HPLC/MS	553			See footnote, ¹¹ O-1126-95.
14. Carbophenothion	GC/MS	625.1	6630 B-2007		See footnote, ⁴ page 27; See footnote, ⁶ p. S73.
	GC	617, 608.3			
15. Chlordane	GC/MS	625.1.	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7; See footnote, ⁴ O-3104-83; See footnote, ⁸ 3M0222.
	GC	617, 608.3			
16. Chlorpropham	GC/MS	625.1	6410 B-2000.		See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	TLC				
17. 2,4-D	HPLC	632.			See footnote, ³ p. 115; See footnote, ⁴ O-3105-83.
	GC/MS	625.1.	6640 B-2006		See footnote, ¹² O-2060-01.
	GC	615			See footnote, ³ p. 7; See footnote, ⁴ O-3105-83; See footnote, ⁸ 3M0222.
18. 4,4'-DDD	HPLC/MS		6630 B-2007 & C-2007	D3086-90, D5812-96(02).	
	GC	617, 608.3			
19. 4,4'-DDE	GC/MS	625.1	6410 B-2000.		See footnote, ³ p. 7; See footnote, ⁴ O-3104-83; See footnote, ⁸ 3M0222.
	GC	617, 608.3	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ¹¹ O-1126-95.
20. 4,4'-DDT	GC/MS	625.1	6410 B-2000		See footnote, ³ p. 7; See footnote, ⁴ O-3104-83; See footnote, ⁸ 3M0222.
	GC	617, 608.3	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	
	GC/MS	625.1	6410 B-2000.		

TABLE ID—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES¹—Continued

Parameter	Method	EPA ^{2,7,10}	Standard methods	ASTM	Other
21. Demeton-O	GC	614, 622			See footnote, ³ p. 25; See footnote, ⁶ p. S51.
	GC/MS	625.1			
22. Demeton-S	GC	614, 622			See footnote, ³ p. 25; See footnote, ⁶ p. S51.
	GC/MS	625.1			
23. Diazinon	GC	507, 614, 622, 1657			See footnote, ³ p. 25; See footnote, ⁴ O-3104-83; See footnote, ⁶ p. S51.
	GC/MS	525.2, 625.1			See footnote, ¹¹ O-1126-95.
24. Dicamba	GC	615			See footnote, ³ p. 115.
	HPLC/MS				See footnote, ¹² O-2060-01.
25. Dichlofenthion	GC	622.1			See footnote, ⁴ page 27; See footnote, ⁶ p. S73.
26. Dichloran	GC	608.2, 617, 608.3	6630 B-2007		See footnote, ³ p. 7.
27. Dicofol	GC	617, 608.3			See footnote, ⁴ O-3104-83.
28. Dieldrin	GC	617, 608.3	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7; See footnote, ⁴ O-3104-83; See footnote, ⁸ 3M0222.
	GC/MS	625.1	6410 B-2000		See footnote, ¹¹ O-1126-95.
29. Dioxathion	GC	614.1, 1657			See footnote, ⁴ page 27; See footnote, ⁶ p. S73.
30. Disulfoton	GC	507, 614, 622, 1657			See footnote, ³ p. 25; See footnote, ⁶ p. S51.
	GC/MS	525.2, 625.1			See footnote, ¹¹ O-1126-95.
31. Diuron	TLC				See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	HPLC	632.			
	HPLC/MS	553			See footnote, ¹² O-2060-01.
32. Endosulfan I	GC	617, 608.3	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7; See footnote, ⁴ O-3104-83; See footnote, ⁸ 3M0222.
	GC/MS	625.1 ⁵	6410 B-2000		See footnote, ¹³ O-2002-01.
33. Endosulfan II	GC	617, 608.3	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7; See footnote, ⁸ 3M0222.
	GC/MS	625.1 ⁵	6410 B-2000		See footnote, ¹³ O-2002-01.
34. Endosulfan Sulfate	GC	617, 608.3	6630 C-2007		See footnote, ⁸ 3M0222.
	GC/MS	625.1	6410 B-2000.		
35. Endrin	GC	505, 508, 617, 1656, 608.3.	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7; See footnote, ⁴ O-3104-83; See footnote, ⁸ 3M0222.
	GC/MS	525.1, 525.2, 625.1 ⁵	6410 B-2000.		
36. Endrin aldehyde	GC	617, 608.3	6630 C-2007		See footnote, ⁸ 3M0222.
	GC/MS	625.1.			
37. Ethion	GC	614, 614.1, 1657			See footnote, ⁴ page 27; See footnote, ⁶ p. S73.
	GC/MS	625.1			See footnote, ¹³ O-2002-01.
38. Fenuron	TLC				See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	HPLC	632.			
39. Fenuron-TCA	HPLC/MS				See footnote, ¹² O-2060-01.
	TLC				See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	HPLC	632.			
40. Heptachlor	GC	505, 508, 617, 1656, 608.3.	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7; See footnote, ⁴ O-3104-83; See footnote, ⁸ 3M0222.
	GC/MS	525.1, 525.2, 625.1	6410 B-2000.		
41. Heptachlor epoxide	GC	617, 608.3	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7; See footnote, ⁴ O-3104-83; See footnote, ⁶ p. S73; See footnote, ⁸ 3M0222.
	GC/MS	625.1	6410 B-2000.		
42. Isodrin	GC	617, 608.3	6630 B-2007 & C-2007		See footnote, ⁴ O-3104-83; See footnote, ⁶ p. S73.
	GC/MS	625.1.			
43. Linuron	GC				See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	HPLC	632.			
	HPLC/MS	553			See footnote, ¹² O-2060-01.
44. Malathion	GC/MS				See footnote, ¹¹ O-1126-95.
	GC	614, 1657	6630 B-2007		See footnote, ³ p. 25; See footnote, ⁶ p. S51.
	GC/MS	625.1			See footnote, ¹¹ O-1126-95.
45. Methiocarb	TLC				See footnote, ³ p. 94; See footnote, ⁶ p. S60.
	HPLC	632.			
	HPLC/MS				See footnote, ¹² O-2060-01.
46. Methoxychlor	GC	505, 508, 608.2, 617, 1656, 608.3.	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7; See footnote, ⁴ O-3104-83; See footnote, ⁸ 3M0222.
	GC/MS	525.1, 525.2, 625.1			See footnote, ¹¹ O-1126-95.

TABLE ID—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES ¹—Continued

Parameter	Method	EPA ^{2,7,10}	Standard methods	ASTM	Other
47. Mexacarbate	TLC	See footnote, ³ p. 94; See footnote, ⁶ p. S60.
	HPLC	632.			
48. Mirex	GC/MS	625.1.	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7; See footnote, ⁴ O-3104-83.
	GC	617, 608.3			
49. Monuron	GC/MS	625.1.			See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	TLC			
50. Monuron-TCA	HPLC	632.			See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	TLC			
51. Neburon	HPLC	632.			See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	TLC			
52. Parathion methyl	HPLC	632.	6630 B-2007		See footnote, ¹² O-2060-01.
	HPLC/MS			See footnote, ⁴ page 27; See footnote, ³ p. 25.
53. Parathion ethyl	GC	614, 622, 1657	6630 B-2007		See footnote, ¹¹ O-1126-95.
	GC/MS	625.1			See footnote, ⁴ page 27; See footnote, ³ p. 25.
54. PCNB	GC	614	6630 B-2007		See footnote, ¹¹ O-1126-95.
	GC/MS	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7.
55. Perthane	GC	608.1, 617, 608.3		D3086-90, D5812-96(02).	See footnote, ⁴ O-3104-83.
56. Prometon	GC	617, 608.3			See footnote, ³ p. 83; See footnote, ⁶ p. S68; See footnote, ⁹ O-3106-93.
	GC	507, 619			
57. Prometryn	GC/MS	525.2, 625.1			See footnote, ¹¹ O-1126-95.
	GC	507, 619			See footnote, ³ p. 83; See footnote, ⁶ p. S68; See footnote, ⁹ O-3106-93.
58. Propazine	GC/MS	525.1, 525.2, 625.1			See footnote, ¹³ O-2002-01.
	GC	507, 619, 1656, 608.3			See footnote, ³ p. 83; See footnote, ⁶ p. S68; See footnote, ⁹ O-3106-93.
59. Propham	GC/MS	525.1, 525.2, 625.1.			See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	TLC			
60. Propoxur	HPLC	632.			See footnote, ¹² O-2060-01.
	HPLC/MS			See footnote, ³ p. 94; See footnote, ⁶ p. S60.
61. Sebumeton	TLC			See footnote, ³ p. 83; See footnote, ⁶ p. S68.
62. Siduron	HPLC	632.			See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	TLC			
63. Simazine	HPLC	632.			See footnote, ¹² O-2060-01.
	HPLC/MS			See footnote, ³ p. 83; See footnote, ⁶ p. S68; See footnote, ⁹ O-3106-93.
64. Strobane	GC	505, 507, 619, 1656, 608.3.			See footnote, ¹¹ O-1126-95.
65. Swep	GC/MS	525.1, 525.2, 625.1	6630 B-2007 & C-2007		See footnote, ³ p. 7.
	GC	617, 608.3			See footnote, ³ p. 104; See footnote, ⁶ p. S64.
	TLC			
66. 2,4,5-T	HPLC	632.	6640 B-2006		See footnote, ³ p. 115; See footnote, ⁴ O-3105-83.
	GC	615			See footnote, ³ p. 115; See footnote, ⁴ O-3105-83.
67. 2,4,5-TP (Silvex)	GC	615	6640 B-2006		See footnote, ³ p. 83; See footnote, ⁶ p. S68.
68. Terbutylazine	GC	619, 1656, 608.3			See footnote, ¹³ O-2002-01.
69. Toxaphene	GC/MS	6630 B-2007 & C-2007	D3086-90, D5812-96(02).	See footnote, ³ p. 7; See footnote, ⁸ See footnote, ⁴ O-3105-83.
	GC	505, 508, 617, 1656, 608.3.			
70. Trifluralin	GC/MS	525.1, 525.2, 625.1	6410 B-2000.		See footnote, ³ p. 7; See footnote, ⁹ O-3106-93.
	GC	508, 617, 627, 1656, 608.3.	6630 B-2007		See footnote, ¹¹ O-1126-95.
	GC/MS	525.2, 625.1			

Table ID notes:

¹ Pesticides are listed in this table by common name for the convenience of the reader. Additional pesticides may be found under Table IC of this section, where entries are listed by chemical name.

² The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at appendix B of this part, Definition and Procedure for the Determination of the Method Detection Limit.

³ Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater. September 1978. U.S. EPA. This EPA publication includes thin-layer chromatography (TLC) methods.

⁴ Methods for the Determination of Organic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A3. 1987. USGS.

⁵ The method may be extended to include α -BHC, γ -BHC, endosulfan I, endosulfan II, and endrin. However, when they are known to exist, Method 608.3 is the preferred method.

⁶ Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency, Supplement to the 15th Edition of *Standard Methods for the Examination of Water and Wastewater*. 1981. American Public Health Association (APHA).

⁷ Each analyst must make an initial, one-time, demonstration of their ability to generate acceptable precision and accuracy with Methods 608.3 and 625.1 in accordance with procedures given in Section 8.2 of each of these methods. Additionally, each laboratory, on an on-going basis, must spike and analyze 5% of all samples analyzed with Method 608.3 or 5% of all samples analyzed with Method 625.1 to monitor and evaluate laboratory data quality in accordance with Sections 8.3 and 8.4 of these methods. When the recovery of any parameter falls outside the warning limits, the analytical results for that parameter in the unspiked sample are suspect. The results should be reported, but cannot be used to demonstrate regulatory compliance. These quality control requirements also apply to the Standard Methods, ASTM Methods, and other methods cited.

⁸ Organochlorine Pesticides and PCBs in Wastewater Using Empore™ Disk. Revised October 28, 1994. 3M Corporation.

⁹ Method O-3106-93 is in Open File Report 94-37, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Triazine and Other Nitrogen-Containing Compounds by Gas Chromatography With Nitrogen Phosphorus Detectors. 1994. USGS.

¹⁰ EPA Methods 608.1, 608.2, 614, 614.1, 615, 617, 619, 622, 622.1, 627, and 632 are found in Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, EPA 821-R-92-002, April 1992, U.S. EPA. EPA Methods 505, 507, 508, 525.1, 531.1 and 553 are in Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, Volume II, EPA 821-R-93-010B, 1993, U.S. EPA. EPA Method 525.2 is in Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry, Revision 2.0, 1995, U.S. EPA. EPA methods 1656 and 1657 are in Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, Volume I, EPA 821-R-93-010A, 1993, U.S. EPA. Methods 608.3 and 625.1 are available at <https://www.epa.gov/cwa-methods/approved-cwa-test-methods-organic-compounds>.

¹¹ Method O-1126-95 is in Open-File Report 95-181, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring. 1995. USGS.

¹² Method O-2060-01 is in Water-Resources Investigations Report 01-4134, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Pesticides in Water by Graphitized Carbon-Based Solid-Phase Extraction and High-Performance Liquid Chromatography/Mass Spectrometry. 2001. USGS.

¹³ Method O-2002-01 is in Water-Resources Investigations Report 01-4098, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of moderate-use pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry. 2001. USGS.

¹⁴ Method O-1121-91 is in Open-File Report 91-519, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of organonitrogen herbicides in water by solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring. 1992. USGS.

* * * * *

TABLE IF—LIST OF APPROVED METHODS FOR PHARMACEUTICAL POLLUTANTS

Pharmaceuticals pollutants	CAS registry No.	Analytical method number
Acetonitrile	75-05-8	1666/1671/D3371/D3695/624.1
n-Amyl acetate	628-63-7	1666/D3695
n-Amyl alcohol	71-41-0	1666/D3695
Benzene	71-43-2	D4763/D3695/502.2/524.2/624.1
n-Butyl-acetate	123-86-4	1666/D3695
tert-Butyl alcohol	75-65-0	1666/624.1
Chlorobenzene	108-90-7	502.2/524.2/624.1
Chloroform	67-66-3	502.2/524.2/551/624.1
o-Dichlorobenzene	95-50-1	1625C/502.2/524.2/624.1
1,2-Dichloroethane	107-06-2	D3695/502.2/524.2/624.1
Diethylamine	109-89-7	1666/1671
Dimethyl sulfoxide	67-68-5	1666/1671
Ethanol	64-17-5	1666/1671/D3695/624.1
Ethyl acetate	141-78-6	1666/D3695/624.1
n-Heptane	142-82-5	1666/D3695
n-Hexane	110-54-3	1666/D3695
Isobutyraldehyde	78-84-2	1666/1667
Isopropanol	67-63-0	1666/D3695
Isopropyl acetate	108-21-4	1666/D3695
Isopropyl ether	108-20-3	1666/D3695
Methanol	67-56-1	1666/1671/D3695/624.1
Methyl Cellosolve® (2-Methoxy ethanol)	109-86-4	1666/1671
Methylene chloride	75-09-2	502.2/524.2/624.1
Methyl formate	107-31-3	1666
4-Methyl-2-pentanone (MIBK)	108-10-1	1624C/1666/D3695/D4763/524.2/624.1
Phenol	108-95-2	D4763
n-Propanol	71-23-8	1666/1671/D3695/624.1
2-Propanone (Acetone)	67-64-1	D3695/D4763/524.2/624.1
Tetrahydrofuran	109-99-9	1666/524.2/624.1
Toluene	108-88-3	D3695/D4763/502.2/524.2/624.1
Triethylamine	121-44-8	1666/1671
Xylenes	(Note 1)	1624C/1666/624.1

Table IF note:

¹ 1624C: *m*-xylene 108-38-3, *o,p*-xylene, E-14095 (Not a CAS number; this is the number provided in the Environmental Monitoring Methods Index [EMMI] database.); 1666: *m,p*-xylene 136777-61-2, *o*-xylene 95-47-6.

TABLE IG—TEST METHODS FOR PESTICIDE ACTIVE INGREDIENTS

[40 CFR part 455]

EPA survey code	Pesticide name	CAS No.	EPA analytical method No.(s) ³
8	Triadimefon	43121-43-3	507/633/525.1/525.2/1656/625.1.

TABLE IG—TEST METHODS FOR PESTICIDE ACTIVE INGREDIENTS—Continued
[40 CFR part 455]

EPA survey code	Pesticide name	CAS No.	EPA analytical method No.(s) ³
12	Dichlorvos	62–73–7	1657/507/622/525.1/525.2/625.1.
16	2,4-D; 2,4-D Salts and Esters [2,4-Dichloro-phenoxy-acetic acid].	94–75–7	1658/515.1/615/515.2/555.
17	2,4-DB; 2,4-DB Salts and Esters [2,4-Dichlorophenoxybutyric acid].	94–82–6	1658/515.1/615/515.2/555.
22	Mevinphos	7786–34–7	1657/507/622/525.1/525.2/625.1.
25	Cyanazine	21725–46–2	629/507/608.3/625.1.
26	Propachlor	1918–16–7	1656/508/608.1/525.1/525.2/608.3/625.1.
27	MCPA; MCPA Salts and Esters [2-Methyl-4-chlorophenoxyacetic acid]	94–74–6	1658/615/555.
30	Dichlorprop; Dichlorprop Salts and Esters [2-(2,4-Dichlorophenoxy) propionic acid].	120–36–5	1658/515.1/615/515.2/555.
31	MCPP; MCPP Salts and Esters [2-(2-Methyl-4-chlorophenoxy) propionic acid].	93–65–2	1658/615/555.
35	TCMTB [2-(Thiocyanomethylthio) benzo-thiazole]	21564–17–0	637.
39	Pronamide	23950–58–5	525.1/525.2/507/633.1/625.1.
41	Propanil	709–98–8	632.1/1656/608.3.
45	Metribuzin	21087–64–9	507/633/525.1/525.2/1656/608.3/625.1.
52	Acephate	30560–19–1	1656/1657/608.3.
53	Acifluorfen	50594–66–6	515.1/515.2/555.
54	Alachlor	15972–60–8	505/507/645/525.1/525.2/1656/608.3/625.1.
55	Aldicarb	116–06–3	531.1.
58	Ametryn	834–12–8	507/619/525.2/625.1.
60	Atrazine	1912–24–9	505/507/619/525.1/525.2/1656/608.3/625.1.
62	Benomyl	17804–35–2	631.
68	Bromacil; Bromacil Salts and Esters	314–40–9	507/633/525.1/525.2/1656/608.3/625.1.
69	Bromoxynil	1689–84–5	1625/1661/625.1.
69	Bromoxynil Octanoate	1689–99–2	1656/608.3.
70	Butachlor	23184–66–9	507/645/525.1/525.2/1656/608.3/625.1.
73	Captafol	2425–06–1	1656/608.3/625.1.
75	Carbaryl [Sevin]	63–25–2	531.1/632/553/625.1.
76	Carbofuran	1563–66–2	531.1/632/625.1.
80	Chloroneb	2675–77–6	1656/508/608.1/525.1/525.2/608.3/625.1.
82	Chlorothalonil	1897–45–6	508/608.2/525.1/525.2/1656/608.3/625.1.
84	Stirofos	961–11–5	1657/507/622/525.1/525.2/625.1.
86	Chlorpyrifos	2921–88–2	1657/508/622/625.1.
90	Fenvalerate	51630–58–1	1660.
103	Diazinon	333–41–5	1657/507/614/622/525.2/625.1.
107	Parathion methyl	298–00–0	1657/614/622/625.1.
110	DCPA [Dimethyl 2,3,5,6-tetrachloro-terephthalate]	1861–32–1	508/608.2/525.1/525.2/515.1 ² /515.2 ² /1656/608.3/625.1.
112	Dinoseb	88–85–7	1658/515.1/615/515.2/555/625.1.
113	Dioxathion	78–34–2	1657/614.1.
118	Nabonate [Disodium cyanodithio-imidocarbonate]	138–93–2	630.1.
119	Diuron	330–54–1	632/553.
123	Endothall	145–73–3	548/548.1.
124	Endrin	72–20–8	1656/505/508/617/525.1/525.2/608.3/625.1.
125	Ethalfuralin	55283–68–6	1656/627/608.3 See footnote 1.
126	Ethion	563–12–2	1657/614/614.1/625.1.
127	Ethoprop	13194–48–4	1657/507/622/525.1/525.2/625.1.
132	Fenarimol	60168–88–9	507/633.1/525.1/525.2/1656/608.3/625.1.
133	Fenthion	55–38–9	1657/622/625.1.
138	Glyphosate [N-(Phosphonomethyl) glycine]	1071–83–6	547.
140	Heptachlor	76–44–8	1656/505/508/617/525.1/525.2/608.3/625.1.
144	Isopropalin	33820–53–0	1656/627/608.3.
148	Linuron	330–55–2	553/632.
150	Malathion	121–75–5	1657/614/625.1.
154	Methamidophos	10265–92–6	1657.
156	Methomyl	16752–77–5	531.1/632.
158	Methoxychlor	72–43–5	1656/505/508/608.2/617/525.1/525.2/608.3/625.1.
172	Nabam	142–59–6	630/630.1.
173	Naled	300–76–5	1657/622/625.1.
175	Norflurazon	27314–13–2	507/645/525.1/525.2/1656/608.3/625.1.
178	Benfluralin	1861–40–1	1656/627/608.3 See footnote 1.
182	Fensulfothion	115–90–2	1657/622/625.1.
183	Disulfoton	298–04–4	1657/507/614/622/525.2/625.1.
185	Phosmet	732–11–6	1657/622.1/625.1.
186	Azinphos Methyl	86–50–0	1657/614/622/625.1.
192	Organo-tin pesticides	12379–54–3	Ind-01/200.7/200.9.
197	Bolstar	35400–43–2	1657/622.

TABLE IG—TEST METHODS FOR PESTICIDE ACTIVE INGREDIENTS—Continued
[40 CFR part 455]

EPA survey code	Pesticide name	CAS No.	EPA analytical method No.(s) ³
203	Parathion	56–38–2	1657/614/625.1.
204	Pendimethalin	40487–42–1	1656.
205	Pentachloronitrobenzene	82–68–8	1656/608.1/617/608.3/625.1.
206	Pentachlorophenol	87–86–5	1625/515.2/555/515.1/525.1/525.2/625.1.
208	Permethrin	52645–53–1	608.2/508/525.1/525.2/1656/1660/608.3 ⁴ /625.1 ⁴ .
212	Phorate	298–02–2	1657/622/625.1.
218	Busan 85 [Potassium dimethyldithiocarbamate]	128–03–0	630/630.1.
219	Busan 40 [Potassium N-hydroxymethyl-N-methyldithiocarbamate]	51026–28–9	630/630.1.
220	KN Methyl [Potassium N-methyl-dithiocarbamate]	137–41–7	630/630.1.
223	Prometon	1610–18–0	507/619/525.2/625.1.
224	Prometryn	7287–19–6	507/619/525.1/525.2/625.1.
226	Propazine	139–40–2	507/619/525.1/525.2/1656/608.3/625.1.
230	Pyrethrin I	121–21–1	1660.
232	Pyrethrin II	121–29–9	1660.
236	DEF [S,S,S-Tributyl phosphorotrithioate]	78–48–8	1657.
239	Simazine	122–34–9	505/507/619/525.1/525.2/1656/608.3/625.1.
241	Carbam-S [Sodium dimethyldithio-carbamate]	128–04–1	630/630.1.
243	Vapam [Sodium methyldithiocarbamate]	137–42–8	630/630.1.
252	Tebuthiuron	34014–18–1	507/525.1/525.2/625.1.
254	Terbacil	5902–51–2	507/633/525.1/525.2/1656/608.3/625.1.
255	Terbufos	13071–79–9	1657/507/614.1/525.1/525.2/625.1.
256	Terbutylazine	5915–41–3	619/1656/608.3.
257	Terbutryn	886–50–0	507/619/525.1/525.2/625.1.
259	Dazomet	533–74–4	630/630.1/1659.
262	Toxaphene	8001–35–2	1656/505/508/617/525.1/525.2/608.3/625.1.
263	Merphos [Tributyl phosphorotrithioate]	150–50–5	1657/507/525.1/525.2/622/625.1.
264	Trifluralin ¹	1582–09–8	1656/508/617/627/525.2/608.3/625.1.
268	Ziram [Zinc dimethyldithiocarbamate]	137–30–4	630/630.1.

Table IG notes:¹ Monitor and report as total Trifluralin.² Applicable to the analysis of DCPA degradates.³ EPA Methods 608.1 through 645, 1645 through 1661, and Ind-01 are available in Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, Volume I, EPA 821–R–93–010A, Revision I, August 1993, U.S. EPA. EPA Methods 200.9 and 505 through 555 are available in Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, Volume II, EPA 821–R–93–010B, August 1993, U.S. EPA. The full text of Methods 608.3, 625.1, and 1625 are provided at appendix A of this part. The full text of Method 200.7 is provided at appendix C of this part. Methods 608.3 and 625.1 are available at <https://www.epa.gov/cwa-methods/approved-cwa-test-methods-organic-compounds>.⁴ Permethrin is not listed within methods 608.3 and 625.1; however, *cis*-permethrin and *trans*-permethrin are listed. Permethrin can be calculated by adding the results of *cis*- and *trans*-permethrin.

TABLE IH—LIST OF APPROVED MICROBIOLOGICAL METHODS FOR AMBIENT WATER

Parameter and units	Method ¹	EPA	Standard methods	AOAC, ASTM, USGS	Other
Bacteria					
1. Coliform (fecal), number per 100 mL or number per gram dry weight.	Most Probable Number (MPN), 5 tube, 3 dilution, or. Membrane filter (MF), ² single step.	p. 132 ³ p. 124 ³	9221 C E–2006. 9222 D–2006 ²⁷	B–0050–85. ⁴	
2. Coliform (fecal) in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or ...	p. 132 ³	9221 C E–2006.		
3. Coliform (total), number per 100 mL.	MF, ² single step ⁵ MPN, 5 tube, 3 dilution, or ...	p. 124 ³ p. 114 ³	9222 D–2006. ²⁷ 9221 B–2006.		
4. Coliform (total), in presence of chlorine, number per 100 mL.	MF, ² single step or two step MPN, 5 tube, 3 dilution, or ...	p. 108 ³ p. 114 ³	9222 B–2006 9221 B–2006.	B–0025–85. ⁴	
5. <i>E. coli</i> , number per 100 mL	MF ² with enrichment MPN, ^{6,8,14} multiple tube, or .. Multiple tube/multiple well, or MF, ^{2,5,6,7,8} two step, or	p. 111 ³ 1103.1 ¹⁹	9222 B–2006. 9221 B.2–2006/9221 F–2006 ^{11,13} . 9223 B–2004 ¹² 9222 B–2006/9222 G–2006, ¹⁸ 9213 D–2007.	991.15 ¹⁰ D–5392–93. ⁹	Colilert [®] , ^{12,16} Colilert-18 [®] , ^{12,15,16}
6. Fecal streptococci, number per 100 mL.	Single step MPN, 5 tube, 3 dilution, or ... MF ² , or	1603, ²⁰ 1604 ²¹ p. 139 ³ p. 136 ³ 9230 B–2007. 9230 C–2007 B–0055–85 ⁴	mColiBlue-24 [®] . ¹⁷

TABLE IH—LIST OF APPROVED MICROBIOLOGICAL METHODS FOR AMBIENT WATER—Continued

Parameter and units	Method ¹	EPA	Standard methods	AOAC, ASTM, USGS	Other
7. Enterococci, number per 100 mL.	Plate count MPN, ^{6,8} multiple tube/multiple well, or MF ^{2,5,6,7,8} two step, or Single step, or Plate count	p. 143. ³ 1106.1 ²³ 1600 ²⁴ p. 143. ³	9230 D-2007 9230 C-2007 9230 C-2007.	D6503-99 ⁹ ... D5259-92. ⁹	Enterolert®. ^{12,22}
Protozoa					
8. <i>Cryptosporidium</i>	Filtration/IMS/FA	1622, ²⁵ 1623. ²⁶			
9. <i>Giardia</i>	Filtration/IMS/FA	1623. ²⁶			

Table IH notes:

¹ The method must be specified when results are reported.

² A 0.45-µm membrane filter (MF) or other pore size certified by the manufacturer to fully retain organisms to be cultivated and to be free of extractables which could interfere with their growth.

³ Microbiological Methods for Monitoring the Environment, Water, and Wastes. EPA/600/8-78/017. 1978. U.S. EPA.

⁴ U.S. Geological Survey Techniques of Water-Resource Investigations, Book 5, Laboratory Analysis, Chapter A4, Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples. 1989. USGS.

⁵ Because the MF technique usually yields low and variable recovery from chlorinated wastewaters, the Most Probable Number method will be required to resolve any controversies.

⁶ Tests must be conducted to provide organism enumeration (density). Select the appropriate configuration of tubes/filtrations and dilutions/volumes to account for the quality, character, consistency, and anticipated organism density of the water sample.

⁷ When the MF method has not been used previously to test waters with high turbidity, large numbers of noncoliform bacteria, or samples that may contain organisms stressed by chlorine, a parallel test should be conducted with a multiple-tube technique to demonstrate applicability and comparability of results.

⁸ To assess the comparability of results obtained with individual methods, it is suggested that side-by-side tests be conducted across seasons of the year with the water samples routinely tested in accordance with the most current Standard Methods for the Examination of Water and Wastewater or EPA alternate test procedure (ATP) guidelines.

⁹ Annual Book of ASTM Standards—Water and Environmental Technology. Section 11.02. 2000, 1999, 1996. ASTM International.

¹⁰ Official Methods of Analysis of AOAC International, 16th Edition, Volume I, Chapter 17. 1995. AOAC International.

¹¹ The multiple-tube fermentation test is used in 9221B.2-2006. Lactose broth may be used in lieu of lauryl tryptose broth (LTB), if at least 25 parallel tests are conducted between this broth and LTB using the water samples normally tested, and this comparison demonstrates that the false-positive rate and false-negative rate for total coliform using lactose broth is less than 10 percent. No requirement exists to run the completed phase on 10 percent of all total coliform-positive tubes on a seasonal basis.

¹² These tests are collectively known as defined enzyme substrate tests, where, for example, a substrate is used to detect the enzyme β-glucuronidase produced by *E. coli*.

¹³ After prior enrichment in a presumptive medium for total coliform using 9221B.2-2006, all presumptive tubes or bottles showing any amount of gas, growth or acidity within 48 h ± 3 h of incubation shall be submitted to 9221F-2006. Commercially available EC-MUG media or EC media supplemented in the laboratory with 50 µg/mL of MUG may be used.

¹⁴ Samples shall be enumerated by the multiple-tube or multiple-well procedure. Using multiple-tube procedures, employ an appropriate tube and dilution configuration of the sample as needed and report the Most Probable Number (MPN). Samples tested with Colilert® may be enumerated with the multiple-well procedures, Quanti-Tray® or Quanti-Tray®/2000, and the MPN calculated from the table provided by the manufacturer.

¹⁵ Colilert-18® is an optimized formulation of the Colilert® for the determination of total coliforms and *E. coli* that provides results within 18 h of incubation at 35 °C, rather than the 24 h required for the Colilert® test, and is recommended for marine water samples.

¹⁶ Descriptions of the Colilert®, Colilert-18®, and Quanti-Tray® may be obtained from IDEXX Laboratories Inc.

¹⁷ A description of the mColiBlue24® test may be obtained from Hach Company.

¹⁸ Subject total coliform positive samples determined by 9222B-2006 or other membrane filter procedure to 9222G-2006 using NA-MUG media.

¹⁹ Method 1103.1: *Escherichia coli* (*E. coli*) in Water by Membrane Filtration Using membrane-Thermotolerant *Escherichia coli* Agar (mTEC), EPA-821-R-10-002. March 2010. U.S. EPA.

²⁰ Method 1603: *Escherichia coli* (*E. coli*) in Water by Membrane Filtration Using Modified membrane-Thermotolerant *Escherichia coli* Agar (Modified mTEC), EPA-821-R-14-010. September 2014. U.S. EPA.

²¹ Preparation and use of MI agar with a standard membrane filter procedure is set forth in the article, Brenner et al. 1993. New Medium for the Simultaneous Detection of Total Coliform and *Escherichia coli* in Water. Appl. Environ. Microbiol. 59:3534-3544 and in Method 1604: Total Coliforms and *Escherichia coli* (*E. coli*) in Water by Membrane Filtration by Using a Simultaneous Detection Technique (MI Medium), EPA 821-R-02-024, September 2002, U.S. EPA.

²² A description of the Enterolert® test may be obtained from IDEXX Laboratories Inc.

²³ Method 1106.1: Enterococci in Water by Membrane Filtration Using membrane-Enterococcus-Esculin Iron Agar (mE-EIA), EPA-821-R-09-015. December 2009. U.S. EPA.

²⁴ Method 1600: Enterococci in Water by Membrane Filtration Using membrane-Enterococcus Indoxyl-β-D-Glucoside Agar (mEI), EPA-821-R-14-011. September 2014. U.S. EPA.

²⁵ Method 1622 uses a filtration, concentration, immunomagnetic separation of oocysts from captured material, immunofluorescence assay to determine concentrations, and confirmation through vital dye staining and differential interference contrast microscopy for the detection of *Cryptosporidium*. Method 1622: *Cryptosporidium* in Water by Filtration/IMS/FA, EPA-821-R-05-001. December 2005. U.S. EPA.

²⁶ Method 1623 uses a filtration, concentration, immunomagnetic separation of oocysts and cysts from captured material, immunofluorescence assay to determine concentrations, and confirmation through vital dye staining and differential interference contrast microscopy for the simultaneous detection of *Cryptosporidium* and *Giardia* oocysts and cysts. Method 1623: *Cryptosporidium* and *Giardia* in Water by Filtration/IMS/FA. EPA-821-R-05-002. December 2005. U.S. EPA.

²⁷ On a monthly basis, at least ten blue colonies from the medium must be verified using Lauryl Tryptose Broth and EC broth, followed by count adjustment based on these results; and representative non-blue colonies should be verified using Lauryl Tryptose Broth. Where possible, verifications should be done from randomized sample sources.

(b) Certain material is incorporated by reference into this part with the approval of the Director of the Federal Register under 5 U.S.C. 552(a) and 1 CFR part 51. All approved material is available for inspection at EPA's Water Docket, EPA West, 1301 Constitution Avenue NW., Room 3334, Washington, DC 20004, Telephone: 202-566-2426, and is available from the sources listed below. It is also available for inspection at the National Archives and Records Administration (NARA). For

information on the availability of this material at NARA, call 202-741-6030, or go to: <https://www.archives.gov/federal-register/cfr/ibr-locations.html>.

* * * * *

(8) * * *

(iv) Method 1600: Enterococci in Water by Membrane Filtration Using membrane-Enterococcus Indoxyl-β-D-Glucoside Agar (mEI). September 2014. EPA-821-R-14-011. Table IA, Note 25; Table IH, Note 24.

(v) Method 1603: *Escherichia coli* (*E. coli*) in Water by Membrane Filtration Using Modified membrane-Thermotolerant *Escherichia coli* Agar (Modified mTEC). September 2014. EPA-821-R-14-010. Table IA, Note 22; Table IH, Note 20.

* * * * *

(xiii) Method 1680: Fecal Coliforms in Sewage Sludge (Biosolids) by Multiple-Tube Fermentation using Lauryl Tryptose Broth (LTB) and EC Medium.

September 2014. EPA-821-R-14-009. Table IA, Note 15.

* * * * *

(xv) Method 1682: *Salmonella* in Sewage Sludge (Biosolids) by Modified Semisolid Rappaport-Vassiliadis (MSRV) Medium. September 2014. EPA 821-R-14-012. Table IA, Note 23.

* * * * *

(10) * * *

(viii) 2120, Color. 2011. Table IB.

(ix) 2130, Turbidity. 2011. Table IB.

(x) 2310, Acidity. 2011. Table IB.

(xi) 2320, Alkalinity. 2011. Table IB.

(xii) 2340, Hardness. 2011. Table IB.

(xiii) 2510, Conductivity. 2011. Table IB.

(xiv) 2540, Solids. 2011. Table IB.

(xv) 2550, Temperature. 2010. Table IB.

(xvi) 3111, Metals by Flame Atomic Absorption Spectrometry. 2011. Table IB.

(xvii) 3112, Metals by Cold-Vapor Atomic Absorption Spectrometry. 2011. Table IB.

(xviii) 3113, Metals by Electrothermal Atomic Absorption Spectrometry. 2010. Table IB.

(xix) 3114, Arsenic and Selenium by Hydride Generation/Atomic Absorption Spectrometry. 2011. Table IB.

(xx) 3120, Metals by Plasma Emission Spectroscopy. 2011. Table IB.

(xxi) 3125, Metals by Inductively Coupled Plasma-Mass Spectrometry. 2011. Table IB.

(xxii) 3500-Al, Aluminum. 2011. Table IB.

(xxiii) 3500-As, Arsenic. 2011. Table IB.

(xxiv) 3500-Ca, Calcium. 2011. Table IB.

(xxv) 3500-Cr, Chromium. 2011. Table IB.

(xxvi) 3500-Cu, Copper. 2011. Table IB.

(xxvii) 3500-Fe, Iron. 2011. Table IB.

(xxviii) 3500-Pb, Lead. 2011. Table IB.

(xxix) 3500-Mn, Manganese. 2011. Table IB.

(xxx) 3500-K, Potassium. 2011. Table IB.

(xxxi) 3500-Na, Sodium. 2011. Table IB.

(xxxii) 3500-V, Vanadium. 2011. Table IB.

(xxxiii) 3500-Zn, Zinc. 2011. Table IB.

(xxxiv) 4110, Determination of Anions by Ion Chromatography. 2011. Table IB.

(xxxv) 4140, Inorganic Anions by Capillary Ion Electrophoresis. 2011. Table IB.

(xxxvi) 4500-B, Boron. 2011. Table IB.

(xxxvii) 4500-Cl⁻, Chloride. 2011. Table IB.

(xxxviii) 4500-Cl, Chlorine (Residual). 2011. Table IB.

(xxxix) 4500-CN⁻, Cyanide. 2011. Table IB.

(xl) 4500-F⁻, Fluoride. 2011. Table IB.

(xli) 4500-H⁺, pH Value. 2011. Table IB.

(xlii) 4500-NH₃, Nitrogen (Ammonia). 2011. Table IB.

(xliii) 4500-NO₂⁻, Nitrogen (Nitrite). 2011. Table IB.

(xliv) 4500-NO₃⁻, Nitrogen (Nitrate). 2011. Table IB.

(xlv) 4500-N_{org}, Nitrogen (Organic). 2011. Table IB.

(xlvi) 4500-O, Oxygen (Dissolved). 2011. Table IB.

(xlvii) 4500-P, Phosphorus. 2011. Table IB.

(xlviii) 4500-SiO₂, Silica. 2011. Table IB.

(xlix) 4500-S²⁻, Sulfide. 2011. Table IB.

(l) 4500-SO₃²⁻, Sulfite. 2011. Table IB.

(li) 4500-SO₄²⁻, Sulfate. 2011. Table IB.

(lii) 5210, Biochemical Oxygen Demand (BOD). 2011. Table IB.

(liii) 5220, Chemical Oxygen Demand (COD). 2011. Table IB.

(liv) 5310, Total Organic Carbon (TOC). 2011. Table IB.

(lv) 5520, Oil and Grease. 2011. Table IB.

(lvi) 5530, Phenols. 2010. Table IB.

(lvii) 5540, Surfactants. 2011. Table IB.

(lviii) 6200, Volatile Organic Compounds. 2011. Table IC.

* * * * *

(lxi) 6440, Polynuclear Aromatic Hydrocarbons. 2005. Table IC.

(lxii) 6630, Organochlorine Pesticides. 2007. Table ID.

(lxiii) 6640, Acidic Herbicide Compounds. 2006. Table ID.

* * * * *

(lxviii) 9222, Membrane Filter Technique for Members of the Coliform Group. 2006. Table IA; Table IH, Note 18.

* * * * *

(15) * * *

(v) ASTM D511-09, Standard Test Methods for Calcium and Magnesium in Water. May 2009. Table IB.

* * * * *

(viii) ASTM D516-11, Standard Test Method for Sulfate Ion in Water, September 2011. Table IB.

(ix) ASTM D858-12, Standard Test Methods for Manganese in Water. September 2012. Table IB.

(x) ASTM D859-10, Standard Test Method for Silica in Water. July 2010. Table IB.

* * * * *

(xii) ASTM D1067-11, Standard Test Methods for Acidity or Alkalinity of Water. April 2011. Table IB.

(xiii) ASTM D1068-10, Standard Test Methods for Iron in Water. October 2010. Table IB.

* * * * *

(xv) ASTM D1126-12, Standard Test Method for Hardness in Water. March 2012. Table IB.

(xvi) ASTM D1179-10, Standard Test Methods for Fluoride Ion in Water. July 2010. Table IB.

(xvii) ASTM D1246-10, Standard Test Method for Bromide Ion in Water. July 2010. Table IB.

* * * * *

(xxii) ASTM D1687-12 (Approved September 1, 2012), Standard Test Methods for Chromium in Water. August 2007. Table IB.

(xxiii) ASTM D1688-12, Standard Test Methods for Copper in Water. September 2012. Table IB.

(xxiv) ASTM D1691-12, Standard Test Methods for Zinc in Water. September 2012. Table IB.

* * * * *

(xxx) ASTM D1976-12, Standard Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy. March 2012. Table IB.

* * * * *

(xxxv) ASTM D3223-12, Standard Test Method for Total Mercury in Water. September 2012. Table IB.

* * * * *

(xxxvii) ASTM D3373-12, Standard Test Method for Vanadium in Water. September 2012. Table IB.

* * * * *

(xxxix) ASTM D3557-12, Standard Test Method for Cadmium in Water. September 2012. Table IB.

* * * * *

(xlii) ASTM D3590-11, Standard Test Methods for Total Kjeldahl Nitrogen in Water. April 2011. Table IB.

* * * * *

(l) ASTM D4382-12, Standard Test Method for Barium in Water, Atomic Absorption Spectrophotometry, Graphite Furnace. September 2012. Table IB.

* * * * *

(lii) ASTM D4658-09, Standard Test Method for Sulfide Ion in Water. May 2009. Table IB.

* * * * *

(lv) ASTM D5257-11, Standard Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography. April 2011. Table IB.

* * * * *

(lviii) ASTM D5673-10, Standard Test Method for Elements in Water by

Inductively Coupled Plasma—Mass Spectrometry. September 2010. Table IB.

(lix) ASTM D5(19)907–13, Standard Test Method for Filterable Matter (Total Dissolved Solids) and Nonfilterable Matter (Total Suspended Solids) in Water. July 2013. Table IB.

* * * * *

(lxi) ASTM. D6508–10, Standard Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte. October 2010. Table IB, Note 54.

* * * * *

(lxiv) ASTM. D7065–11, Standard Test Method for Determination of Nonylphenol, Bisphenol A, *p*-tert-Octylphenol, Nonylphenol Monoethoxylate and Nonylphenol Diethoxylate in Environmental Waters by Gas Chromatography Mass Spectrometry. July 2011. Table IB.

* * * * *

(lxvi) ASTM. D7284–13, Standard Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection. July 2013. Table IB.

* * * * *

(lxviii) ASTM. D7511–12, Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection. January 2012. Table IB.

* * * * *

(19) * * *

(vii) Method 10206, Hach Company TNTplus 835/836 Nitrate Method 10206, Spectrophotometric Measurement of Nitrate in Water and Wastewater. Revision 2.1, January 10, 2013. Table IB, Note 75.

(viii) Method 10242, Hach Company TNTplus 880 Total Kjeldahl Nitrogen Method 10242, Simplified Spectrophotometric Measurement of Total Kjeldahl Nitrogen in Water and Wastewater. Revision 1.1, January 10, 2013. Table IB, Note 76.

* * * * *

(20) * * *

(i) Colilert. 2013. Table IA, Notes 17 and 18; Table IH, Notes 14, 15 and 16.

(ii) Colilert-18. 2013. Table IA, Notes 17 and 18; Table IH, Notes 14, 15 and 16.

(iii) Enterolert. 2013. Table IA, Note 24; Table IH, Note 12.

(iv) Quanti-Tray Insert and Most Probable Number (MPN) Table. 2013. Table IA, Note 18; Table IH, Notes 14 and 16.

* * * * *

(25) * * *

(i) NCASI Method TNTP–W10900, Total Nitrogen and Total Phosphorus in Pulp and Paper Biologically Treated Effluent by Alkaline Persulfate Digestion. June 2011. Table IB, Note 77.

(ii) NCASI Technical Bulletin No. 253, An Investigation of Improved Procedures for Measurement of Mill Effluent and Receiving Water Color. December 1971. Table IB, Note 18.

(iii) NCASI Technical Bulletin No. 803, An Update of Procedures for the Measurement of Color in Pulp Mill Wastewaters. May 2000. Table IB, Note 18.

(26) The Nitrate Elimination Co., Inc. (NECi), 334 Hecla St., Lake Linden MI 49945.

(i) NECi Method N07–0003, Method for Nitrate Reductase Nitrate-Nitrogen Analysis. Revision 9.0. March 2014. Table IB, Note 73.

(ii) [Reserved]

* * * * *

(34) Timberline Instruments, LLC, 1880 South Flatiron Ct., Unit I, Boulder CO 80301.

(i) Timberline Amonia-001, Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Conductivity Cell Analysis. June 24, 2011. Table IB, Note 74.

(ii) [Reserved]

(35) U.S. Geological Survey (USGS), U.S. Department of the Interior, Reston, Virginia. Available from USGS Books and Open-File Reports (OFR) Section, Federal Center, Box 25425, Denver, CO 80225.

(i) Colorimetric determination of nitrate plus nitrite in water by enzymatic reduction, automated discrete analyzer methods. U.S. Geological Survey Techniques and Methods, Book 5—Laboratory Analysis, Section B—Methods of the National Water Quality Laboratory, Chapter 8. 2011. Table IB, Note 72.

(ii) Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, editors, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A1. 1979. Table IB, Note 8.

(iii) Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A1. 1989. Table IB, Note 2.

(iv) Methods for the Determination of Organic Substances in Water and Fluvial Sediments. Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A3. 1987. Table IB, Note 24; Table ID, Note 4.

(v) OFR 76–177, Selected Methods of the U.S. Geological Survey of Analysis of Wastewaters. 1976. Table IE, Note 2.

(vi) OFR 91–519, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Organonitrogen Herbicides in Water by Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry With Selected-Ion Monitoring. 1992. Table ID, Note 14.

(vii) OFR 92–146, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Total Phosphorus by a Kjeldahl Digestion Method and an Automated Colorimetric Finish That Includes Dialysis. 1992. Table IB, Note 48.

(viii) OFR 93–125, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments. 1993. Table IB, Note 51; Table IC, Note 9.

(ix) OFR 93–449, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Chromium in Water by Graphite Furnace Atomic Absorption Spectrophotometry. 1993. Table IB, Note 46.

(x) OFR 94–37, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Triazine and Other Nitrogen-containing Compounds by Gas Chromatography With Nitrogen Phosphorus Detectors. 1994. Table ID, Note 9.

(xi) OFR 95–181, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Pesticides in Water by C–18 Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry With Selected-Ion Monitoring. 1995. Table ID, Note 11.

(xii) OFR 97–198, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Molybdenum in Water by Graphite Furnace Atomic Absorption Spectrophotometry. 1997. Table IB, Note 47.

(xiii) OFR 98–165, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Elements in Whole-Water Digests Using Inductively Coupled Plasma-Optical Emission Spectrometry and Inductively Coupled Plasma-Mass Spectrometry. 1998. Table IB, Note 50.

(xiv) OFR 98–639, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—

Determination of Arsenic and Selenium in Water and Sediment by Graphite Furnace—Atomic Absorption Spectrometry. 1999. Table IB, Note 49.

(xv) OFR 00–170, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Ammonium Plus Organic Nitrogen by a Kjeldahl Digestion Method and an Automated Photometric Finish that Includes Digest Cleanup by Gas Diffusion. 2000. Table IB, Note 45.

(xvi) Techniques and Methods Book 5–B1, Determination of Elements in Natural-Water, Biota, Sediment and Soil Samples Using Collision/Reaction Cell Inductively Coupled Plasma-Mass Spectrometry. Chapter 1, Section B, Methods of the National Water Quality Laboratory, Book 5, Laboratory Analysis. 2006. Table IB, Note 70.

(xvii) U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Laboratory

Analysis, Chapter A4, Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples. 1989. Table IA, Note 4; Table IH, Note 4.

(xviii) Water-Resources Investigation Report 01–4098, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Moderate-Use Pesticides and Selected Degradates in Water by C–18 Solid-Phase Extraction and Gas Chromatography/Mass Spectrometry. 2001. Table ID, Note 13.

(xix) Water-Resources Investigations Report 01–4132, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Organic Plus Inorganic Mercury in Filtered and Unfiltered Natural Water With Cold Vapor-Atomic Fluorescence Spectrometry. 2001. Table IB, Note 71.

(xx) Water-Resources Investigation Report 01–4134, Methods of Analysis by

the U.S. Geological Survey National Water Quality Laboratory—Determination of Pesticides in Water by Graphitized Carbon-Based Solid-Phase Extraction and High-Performance Liquid Chromatography/Mass Spectrometry. 2001. Table ID, Note 12.

(xxi) Water Temperature—Influential Factors, Field Measurement and Data Presentation, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 1, Chapter D1. 1975. Table IB, Note 32.

* * * * *

(c) Under certain circumstances, the Director may establish limitations on the discharge of a parameter for which there is no test procedure in this part or in 40 CFR parts 405 through 499. In these instances the test procedure shall be specified by the Director.

* * * * *

(e) * * *

TABLE II—REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter number/name	Container ¹	Preservation ^{2 3}	Maximum holding time ⁴
Table IA—Bacterial Tests			
1–5. Coliform, total, fecal, and <i>E. coli</i> .	PA, G	Cool, <10 °C, 0.008% Na ₂ S ₂ O ₃ ⁵	8 hours. ^{22 23}
6. Fecal streptococci	PA, G	Cool, <10 °C, 0.008% Na ₂ S ₂ O ₃ ⁵	8 hours. ²²
7. Enterococci	PA, G	Cool, <10 °C, 0.008% Na ₂ S ₂ O ₃ ⁵	8 hours. ²²
8. <i>Salmonella</i>	PA, G	Cool, <10 °C, 0.008% Na ₂ S ₂ O ₃ ⁵	8 hours. ²²
Table IA—Aquatic Toxicity Tests			
9–12. Toxicity, acute and chronic ..	P, FP, G	Cool, ≤6 °C ¹⁶	36 hours.
Table IB—Inorganic Tests			
1. Acidity	P, FP, G	Cool, ≤6 °C ¹⁸	14 days.
2. Alkalinity	P, FP, G	Cool, ≤6 °C ¹⁸	14 days.
4. Ammonia	P, FP, G	Cool, ≤6 °C, ¹⁸ H ₂ SO ₄ to pH <2	28 days.
9. Biochemical oxygen demand	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.
10. Boron	P, FP, or Quartz	HNO ₃ to pH <2	6 months.
11. Bromide	P, FP, G	None required	28 days.
14. Biochemical oxygen demand, carbonaceous.	P, FP G	Cool, ≤6 °C ¹⁸	48 hours.
15. Chemical oxygen demand	P, FP, G	Cool, ≤6 °C, ¹⁸ H ₂ SO ₄ to pH <2	28 days.
16. Chloride	P, FP, G	None required	28 days.
17. Chlorine, total residual	P, G	None required	Analyze within 15 minutes.
21. Color	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.
23–24. Cyanide, total or available (or CATC) and free.	P, FP, G	Cool, ≤6 °C, ¹⁸ NaOH to pH >10, ^{5 6} reducing agent if oxidizer present.	14 days.
25. Fluoride	P	None required	28 days.
27. Hardness	P, FP, G	HNO ₃ or H ₂ SO ₄ to pH <2	6 months.
28. Hydrogen ion (pH)	P, FP, G	None required	Analyze within 15 minutes.
31, 43. Kjeldahl and organic N	P, FP, G	Cool, ≤6 °C, ¹⁸ H ₂ SO ₄ to pH <2	28 days.
Table IB—Metals ⁷			
18. Chromium VI	P, FP, G	Cool, ≤6 °C, ¹⁸ pH = 9.3–9.7 ²⁰	28 days.
35. Mercury (CVAA)	P, FP, G	HNO ₃ to pH <2	28 days.
35. Mercury (CVAFS)	FP, G; and FP-lined cap ¹⁷	5 mL/L 12N HCl or 5 mL/L BrCl ¹⁷	90 days. ¹⁷
3, 5–8, 12, 13, 19, 20, 22, 26, 29, 30, 32–34, 36, 37, 45, 47, 51, 52, 58–60, 62, 63, 70–72, 74, 75. Metals, except boron, chromium VI, and mercury.	P, FP, G	HNO ₃ to pH <2, or at least 24 hours prior to analysis ¹⁹ .	6 months.

TABLE II—REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES—Continued

Parameter number/name	Container ¹	Preservation ^{2 3}	Maximum holding time ⁴
38. Nitrate	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.
39. Nitrate-nitrite	P, FP, G	Cool, ≤6 °C, ¹⁸ H ₂ SO ₄ to pH <2	28 days.
40. Nitrite	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.
41. Oil and grease	G	Cool to ≤6 °C, ¹⁸ HCl or H ₂ SO ₄ to pH <2.	28 days.
42. Organic Carbon	P, FP, G	Cool to ≤6 °C, ¹⁸ HCl, H ₂ SO ₄ , or H ₃ PO ₄ to pH <2.	28 days.
44. Orthophosphate	P, FP, G	Cool, to ≤6 °C ^{18 24}	Filter within 15 minutes; Analyze within 48 hours.
46. Oxygen, Dissolved Probe	G, Bottle and top	None required	Analyze within 15 minutes.
47. Winkler	G, Bottle and top	Fix on site and store in dark	8 hours.
48. Phenols	G	Cool, ≤6 °C, ¹⁸ H ₂ SO ₄ to pH <2	28 days.
49. Phosphorous (elemental)	G	Cool, ≤6 °C ¹⁸	48 hours.
50. Phosphorous, total	P, FP, G	Cool, ≤6 °C, ¹⁸ H ₂ SO ₄ to pH <2	28 days.
53. Residue, total	P, FP, G	Cool, ≤6 °C ¹⁸	7 days.
54. Residue, Filterable	P, FP, G	Cool, ≤6 °C ¹⁸	7 days.
55. Residue, Nonfilterable (TSS) ...	P, FP, G	Cool, ≤6 °C ¹⁸	7 days.
56. Residue, Settleable	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.
57. Residue, Volatile	P, FP, G	Cool, ≤6 °C ¹⁸	7 days.
61. Silica	P or Quartz	Cool, ≤6 °C ¹⁸	28 days.
64. Specific conductance	P, FP, G	Cool, ≤6 °C ¹⁸	28 days.
65. Sulfate	P, FP, G	Cool, ≤6 °C ¹⁸	28 days.
66. Sulfide	P, FP, G	Cool, ≤6 °C, ¹⁸ add zinc acetate plus sodium hydroxide to pH >9.	7 days.
67. Sulfite	P, FP, G	None required	Analyze within 15 minutes.
68. Surfactants	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.
69. Temperature	P, FP, G	None required	Analyze within 15 minutes.
73. Turbidity	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.

Table IC—Organic Tests ⁸

13, 18–20, 22, 24, 25, 27, 28, 34–37, 39–43, 45–47, 56, 76, 104, 105, 108–111, 113. Purgeable Halocarbons.	G, FP-lined septum	Cool, ≤6 °C, ¹⁸ 0.008% Na ₂ S ₂ O ₃ , ⁵ HCl to pH 2.	14 days.
26. 2-Chloroethylvinyl ether	G, FP-lined septum	Cool, ≤6 °C, ¹⁸ 0.008% Na ₂ S ₂ O ₃ ⁵	14 days.
6, 57, 106. Purgeable aromatic hydrocarbons.	G, FP-lined septum	Cool, ≤6 °C, ¹⁸ 0.008% Na ₂ S ₂ O ₃ , ⁵ HCl to pH 2 ⁹ .	14 days. ⁹
3, 4. Acrolein and acrylonitrile	G, FP-lined septum	Cool, ≤6 °C, ¹⁸ 0.008% Na ₂ S ₂ O ₃ , pH to 4–5 ¹⁰ .	14 days. ¹⁰
23, 30, 44, 49, 53, 77, 80, 81, 98, 100, 112. Phenols ¹¹ .	G, FP-lined cap	Cool, ≤6 °C, ¹⁸ 0.008% Na ₂ S ₂ O ₃ ..	7 days until extraction, 40 days after extraction.
7, 38. Benzidines ^{11 12}	G, FP-lined cap	Cool, ≤6 °C, ¹⁸ 0.008% Na ₂ S ₂ O ₃ ⁵	7 days until extraction. ¹³
14, 17, 48, 50–52. Phthalate esters ¹¹ .	G, FP-lined cap	Cool, ≤6 °C ¹⁸	7 days until extraction, 40 days after extraction.
82–84. Nitrosamines ^{11 14}	G, FP-lined cap	Cool, ≤6 °C, ¹⁸ store in dark, 0.008% Na ₂ S ₂ O ₃ ⁵ .	7 days until extraction, 40 days after extraction.
88–94. PCBs ¹¹	G, FP-lined cap	Cool, ≤6 °C ¹⁸	1 year until extraction, 1 year after extraction.
54, 55, 75, 79. Nitroaromatics and isophorone ¹¹ .	G, FP-lined cap	Cool, ≤6 °C, ¹⁸ store in dark, 0.008% Na ₂ S ₂ O ₃ ⁵ .	7 days until extraction, 40 days after extraction.
1, 2, 5, 8–12, 32, 33, 58, 59, 74, 78, 99, 101. Polynuclear aromatic hydrocarbons ¹¹ .	G, FP-lined cap	Cool, ≤6 °C, ¹⁸ store in dark, 0.008% Na ₂ S ₂ O ₃ ⁵ .	7 days until extraction, 40 days after extraction.
15, 16, 21, 31, 87. Haloethers ¹¹ ...	G, FP-lined cap	Cool, ≤6 °C, ¹⁸ 0.008% Na ₂ S ₂ O ₃ ⁵	7 days until extraction, 40 days after extraction.
29, 35–37, 63–65, 107. Chlorinated hydrocarbons ¹¹ .	G, FP-lined cap	Cool, ≤6 °C ¹⁸	7 days until extraction, 40 days after extraction.
60–62, 66–72, 85, 86, 95–97, 102, 103. CDDs/CDFs ¹¹ .	G	See footnote 11	See footnote 11.
Aqueous Samples: Field and Lab Preservation.	G	Cool, ≤6 °C, ¹⁸ 0.008% Na ₂ S ₂ O ₃ , ⁵ pH <9.	1 year.
Solids and Mixed-Phase Samples: Field Preservation.	G	Cool, ≤6 °C ¹⁸	7 days.
Tissue Samples: Field Preservation.	G	Cool, ≤6 °C ¹⁸	24 hours.
Solids, Mixed-Phase, and Tissue Samples: Lab Preservation.	G	Freeze, ≤ –10 °C	1 year.
114–118. Alkylated phenols	G	Cool, <6 °C, H ₂ SO ₄ to pH <2	28 days until extraction, 40 days after extraction.

TABLE II—REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES—Continued

Parameter number/name	Container ¹	Preservation ^{2 3}	Maximum holding time ⁴
119. Adsorbable Organic Halides (AOX).	G	Cool, <6 °C, 0.008% Na ₂ S ₂ O ₃ , HNO ₃ to pH <2.	Hold <i>at least</i> 3 days, but not more than 6 months.
120. Chlorinated Phenolics	G, FP-lined cap	Cool, <6 °C, 0.008% Na ₂ S ₂ O ₃ , H ₂ SO ₄ to pH <2.	30 days until acetylation, 30 days after acetylation.
Table ID—Pesticides Tests			
1–70. Pesticides ¹¹	G, FP-lined cap	Cool, ≤6 °C, ¹⁸ pH 5–9 ¹⁵	7 days until extraction, 40 days after extraction.
Table IE—Radiological Tests			
1–5. Alpha, beta, and radium	P, FP, G	HNO ₃ to pH <2	6 months.
Table IH—Bacterial Tests			
1–4. Coliform, total, fecal	PA, G	Cool, <10 °C, 0.008% Na ₂ S ₂ O ₃ ⁵	8 hours. ^{22 23}
5. <i>E. coli</i>	PA, G	Cool, <10 °C, 0.008% Na ₂ S ₂ O ₃ ⁵	8 hours. ²²
6. Fecal streptococci	PA, G	Cool, <10 °C, 0.008% Na ₂ S ₂ O ₃ ⁵	8 hours. ²²
7. Enterococci	PA, G	Cool, <10 °C, 0.008% Na ₂ S ₂ O ₃ ⁵	8 hours. ²²
Table IH—Protozoan Tests			
8. <i>Cryptosporidium</i>	LDPE; field filtration	1–10 °C	96 hours. ²¹
9. <i>Giardia</i>	LDPE; field filtration	1–10 °C	96 hours. ²¹

¹ “P” is for polyethylene; “FP” is fluoropolymer (polytetrafluoroethylene (PTFE); Teflon®), or other fluoropolymer, unless stated otherwise in this Table II; “G” is glass; “PA” is any plastic that is made of a sterilizable material (polypropylene or other autoclavable plastic); “LDPE” is low density polyethylene.

² Except where noted in this Table II and the method for the parameter, preserve each grab sample within 15 minutes of collection. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sample; see 40 CFR 122.21(g)(7)(i) or 40 CFR part 403, appendix E), refrigerate the sample at ≤6 °C during collection unless specified otherwise in this Table II or in the method(s). For a composite sample to be split into separate aliquots for preservation and/or analysis, maintain the sample at ≤6 °C, unless specified otherwise in this Table II or in the method(s), until collection, splitting, and preservation is completed. Add the preservative to the sample container prior to sample collection when the preservative will not compromise the integrity of a grab sample, a composite sample, or aliquot split from a composite sample within 15 minutes of collection. If a composite measurement is required but a composite sample would compromise sample integrity, individual grab samples must be collected at prescribed time intervals (e.g., 4 samples over the course of a day, at 6-hour intervals). Grab samples must be analyzed separately and the concentrations averaged. Alternatively, grab samples may be collected in the field and composited in the laboratory if the compositing procedure produces results equivalent to results produced by arithmetic averaging of results of analysis of individual grab samples. For examples of laboratory compositing procedures, see EPA Method 1664 Rev. A (oil and grease) and the procedures at 40 CFR 141.24(f)(14)(iv) and (v) (volatile organics).

³ When any sample is to be shipped by common carrier or sent via the U.S. Postal Service, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirement of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO₃) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H₂SO₄) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

⁴ Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before the start of analysis and still be considered valid. Samples may be held for longer periods only if the permittee or monitoring laboratory have data on file to show that, for the specific types of samples under study, the analytes are stable for the longer time, and has received a variance from the Regional ATP Coordinator under § 136.3(e). For a grab sample, the holding time begins at the time of collection. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR part 403, appendix E), the holding time begins at the time of the end of collection of the composite sample. For a set of grab samples composited in the field or laboratory, the holding time begins at the time of collection of the last grab sample in the set. Some samples may not be stable for the maximum time period given in the table. A permittee or monitoring laboratory is obligated to hold the sample for a shorter time if it knows that a shorter time is necessary to maintain sample stability. See § 136.3(e) for details. The date and time of collection of an individual grab sample is the date and time at which the sample is collected. For a set of grab samples to be composited, and that are all collected on the same calendar date, the date of collection is the date on which the samples are collected. For a set of grab samples to be composited, and that are collected across two calendar dates, the date of collection is the dates of the two days; e.g., November 14–15. For a composite sample collected automatically on a given date, the date of collection is the date on which the sample is collected. For a composite sample collected automatically, and that is collected across two calendar dates, the date of collection is the dates of the two days; e.g., November 14–15. For static-renewal toxicity tests, each grab or composite sample may also be used to prepare test solutions for renewal at 24 h, 48 h, and/or 72 h after first use, if stored at 0–6 °C, with minimum head space.

⁵ ASTM D7365–09a specifies treatment options for samples containing oxidants (e.g., chlorine) for cyanide analyses. Also, Section 9060A of Standard Methods for the Examination of Water and Wastewater (20th and 21st editions) addresses dechlorination procedures for microbiological analyses.

⁶ Sampling, preservation and mitigating interferences in water samples for analysis of cyanide are described in ASTM D7365–09a. There may be interferences that are not mitigated by the analytical test methods or D7365–09a. Any technique for removal or suppression of interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide through quality control measures described in the analytical test method. Any removal or suppression technique not described in D7365–09a or the analytical test method must be documented along with supporting data.

⁷ For dissolved metals, filter grab samples within 15 minutes of collection and before adding preservatives. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR part 403, appendix E), filter the sample within 15 minutes after completion of collection and before adding preservatives. If it is known or suspected that dissolved sample integrity will be compromised during collection of a composite sample collected automatically over time (e.g., by interchange of a metal between dissolved and suspended forms), collect and filter grab samples to be composited (footnote 2) in place of a composite sample collected automatically.

⁸ Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

⁹ If the sample is not adjusted to pH 2, then the sample must be analyzed within seven days of sampling.

¹⁰ The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

¹¹ When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity (*i.e.*, use all necessary preservatives and hold for the shortest time listed). When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to $\leq 6^{\circ}\text{C}$, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6–9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (regarding the requirement for thiosulfate reduction), and footnotes 12, 13 (regarding the analysis of benzidine).

¹² If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 ± 0.2 to prevent rearrangement to benzidine.

¹³ Extracts may be stored up to 30 days at $< 0^{\circ}\text{C}$.

¹⁴ For the analysis of diphenylnitrosamine, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ and adjust pH to 7–10 with NaOH within 24 hours of sampling.

¹⁵ The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$.

¹⁶ Place sufficient ice with the samples in the shipping container to ensure that ice is still present when the samples arrive at the laboratory. However, even if ice is present when the samples arrive, immediately measure the temperature of the samples and confirm that the preservation temperature maximum has not been exceeded. In the isolated cases where it can be documented that this holding temperature cannot be met, the permittee can be given the option of on-site testing or can request a variance. The request for a variance should include supportive data which show that the toxicity of the effluent samples is not reduced because of the increased holding temperature. Aqueous samples must not be frozen. Hand-delivered samples used on the day of collection do not need to be cooled to 0 to 6°C prior to test initiation.

¹⁷ Samples collected for the determination of trace level mercury ($< 100\text{ ng/L}$) using EPA Method 1631 must be collected in tightly-capped fluoropolymer or glass bottles and preserved with BrCl or HCl solution within 48 hours of sample collection. The time to preservation may be extended to 28 days if a sample is oxidized in the sample bottle. A sample collected for dissolved trace level mercury should be filtered in the laboratory within 24 hours of the time of collection. However, if circumstances preclude overnight shipment, the sample should be filtered in a designated clean area in the field in accordance with procedures given in Method 1669. If sample integrity will not be maintained by shipment to and filtration in the laboratory, the sample must be filtered in a designated clean area in the field within the time period necessary to maintain sample integrity. A sample that has been collected for determination of total or dissolved trace level mercury must be analyzed within 90 days of sample collection.

¹⁸ Aqueous samples must be preserved at $\leq 6^{\circ}\text{C}$, and should not be frozen unless data demonstrating that sample freezing does not adversely impact sample integrity is maintained on file and accepted as valid by the regulatory authority. Also, for purposes of NPDES monitoring, the specification of “ $\leq 6^{\circ}\text{C}$ ” is used in place of the “ 4°C ” and “ $< 4^{\circ}\text{C}$ ” sample temperature requirements listed in some methods. It is not necessary to measure the sample temperature to three significant figures (1/100th of 1 degree); rather, three significant figures are specified so that rounding down to 6°C may not be used to meet the $\leq 6^{\circ}\text{C}$ requirement. The preservation temperature does not apply to samples that are analyzed immediately (less than 15 minutes).

¹⁹ An aqueous sample may be collected and shipped without acid preservation. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. If the sample must be analyzed within 24 hours of collection, add the acid immediately (see footnote 2). Soil and sediment samples do not need to be preserved with acid. The allowances in this footnote supersede the preservation and holding time requirements in the approved metals methods.

²⁰ To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed.

²¹ Holding time is calculated from time of sample collection to elution for samples shipped to the laboratory in bulk and calculated from the time of sample filtration to elution for samples filtered in the field.

²² Sample analysis should begin as soon as possible after receipt; sample incubation must be started no later than 8 hours from time of collection.

²³ For fecal coliform samples for sewage sludge (biosolids) only, the holding time is extended to 24 hours for the following sample types using either EPA Method 1680 (LTB–EC) or 1681 (A–1): Class A composted, Class B aerobically digested, and Class B anaerobically digested.

²⁴ The immediate filtration requirement in orthophosphate measurement is to assess the dissolved or bio-available form of orthophosphorus (*i.e.*, that which passes through a 0.45-micron filter), hence the requirement to filter the sample immediately upon collection (*i.e.*, within 15 minutes of collection).

■ 5. Section 136.4 is amended by revising paragraphs (a) introductory text, (b), and (c) to read as follows:

§ 136.4 Application for and approval of alternate test procedures for nationwide use.

(a) A written application for review of an alternate test procedure (alternate method) for nationwide use may be made by letter via email or by hard copy in triplicate to the National Alternate Test Procedure (ATP) Program Coordinator (National Coordinator), Office of Science and Technology (4303T), Office of Water, U.S. Environmental Protection Agency, 1200 Pennsylvania Ave. NW., Washington, DC 20460. Any application for an ATP under this paragraph (a) shall:

* * * * *

(b) The National Coordinator may request additional information and analyses from the applicant in order to evaluate whether the alternate test

procedure satisfies the applicable requirements of this part.

(c) *Approval for nationwide use.* (1) After a review of the application and any additional analyses requested from the applicant, the National Coordinator will notify the applicant, in writing, of whether the National Coordinator will recommend approval or disapproval of the alternate test procedure for nationwide use in CWA programs. If the application is not recommended for approval, the National Coordinator may specify what additional information might lead to a reconsideration of the application and notify the Regional Alternate Test Procedure Coordinators of the disapproval recommendation. Based on the National Coordinator's recommended disapproval of a proposed alternate test procedure and an assessment of any current approvals for limited uses for the unapproved method, the Regional ATP Coordinator

may decide to withdraw approval of the method for limited use in the Region.

(2) Where the National Coordinator has recommended approval of an applicant's request for nationwide use of an alternate test procedure, the National Coordinator will notify the applicant. The National Coordinator will also notify the Regional ATP Coordinators that they may consider approval of this alternate test procedure for limited use in their Regions based on the information and data provided in the application until the alternate test procedure is approved by publication in a final rule in the **Federal Register**.

(3) EPA will propose to amend this part to include the alternate test procedure in § 136.3. EPA shall make available for review all the factual bases for its proposal, including the method, any performance data submitted by the applicant and any available EPA analysis of those data.

(4) Following public comment, EPA shall publish in the **Federal Register** a

final decision on whether to amend this part to include the alternate test procedure as an approved analytical method for nationwide use.

(5) Whenever the National Coordinator has recommended approval of an applicant's ATP request for nationwide use, any person may request an approval of the method for limited use under § 136.5 from the EPA Region.

■ 6. Section 136.5 is amended by revising paragraphs (a), (b), (c)(1), and (d) to read as follows:

§ 136.5 Approval of alternate test procedures for limited use.

(a) Any person may request the Regional ATP Coordinator to approve the use of an alternate test procedure in the Region.

(b) When the request for the use of an alternate test procedure concerns use in a State with an NPDES permit program approved pursuant to section 402 of the Act, the requestor shall first submit an application for limited use to the Director of the State agency having responsibility for issuance of NPDES permits within such State (*i.e.*, permitting authority). The Director will forward the application to the Regional ATP Coordinator with a recommendation for or against approval.

(c) * * *

(1) Provide the name and address of the applicant and the applicable ID number of the existing or pending permit(s) and issuing agency for which use of the alternate test procedure is requested, and the discharge serial number.

* * * * *

(d) *Approval for limited use.* (1) The Regional ATP Coordinator will review the application and notify the applicant and the appropriate State agency of approval or rejection of the use of the alternate test procedure. The approval may be restricted to use only with respect to a specific discharge or facility (and its laboratory) or, at the discretion of the Regional ATP Coordinator, to all dischargers or facilities (and their associated laboratories) specified in the approval for the Region. If the application is not approved, the Regional ATP Coordinator shall specify what additional information might lead to a reconsideration of the application.

(2) The Regional ATP Coordinator will forward a copy of every approval and rejection notification to the National Alternate Test Procedure Coordinator.

■ 7. In § 136.6:

■ a. Revise paragraphs (b)(1) and (2) introductory text.

■ b. Remove paragraph (b)(4)(xvii).

■ c. Redesignate paragraphs (b)(4)(xviii) through the first occurrence of (xxii) as paragraphs (b)(4)(xvii) through (xxi), respectively and retaining the second occurrence of paragraph (b)(4)(xxii).

■ d. Add paragraph (c).

The revisions and addition read as follows:

§ 136.6 Method modifications and analytical requirements.

* * * * *

(b) *Method modifications.* (1) If the underlying chemistry and determinative technique in a modified method are essentially the same as an approved Part 136 method, then the modified method is an equivalent and acceptable alternative to the approved method provided the requirements of this section are met. However, those who develop or use a modification to an approved (Part 136) method must document that the performance of the modified method, in the matrix to which the modified method will be applied, is equivalent to the performance of the approved method. If such a demonstration cannot be made and documented, then the modified method is not an acceptable alternative to the approved method. Supporting documentation must, if applicable, include the routine initial demonstration of capability and ongoing QC including determination of precision and accuracy, detection limits, and matrix spike recoveries. Initial demonstration of capability typically includes analysis of four replicates of a mid-level standard and a method detection limit study. Ongoing quality control typically includes method blanks, mid-level laboratory control samples, and matrix spikes (QC is as specified in the method). The method is considered equivalent if the quality control requirements in the reference method are achieved. Where the laboratory is using a vendor-supplied method, it is the QC criteria in the reference method, not the vendor's method, that must be met to show equivalency. Where a sample preparation step is required (*i.e.*, digestion, distillation), QC tests are to be run using standards treated in the same way as the samples. The method user's Standard Operating Procedure (SOP) must clearly document the modifications made to the reference method. Examples of allowed method modifications are listed in this section. If the method user is uncertain whether a method modification is allowed, the Regional ATP Coordinator or Director should be contacted for approval *prior* to implementing the modification. The method user should also complete

necessary performance checks to verify that acceptable performance is achieved with the method modification *prior* to analyses of compliance samples.

(2) *Requirements.* The modified method must meet or exceed performance of the approved method(s) for the analyte(s) of interest, as documented by meeting the initial and ongoing quality control requirements in the method.

* * * * *

(c) The permittee must notify their permitting authority of the intent to use a modified method. Such notification should be of the form "Method xxx has been modified within the flexibility allowed in 40 CFR 136.6." The permittee may indicate the specific paragraph of § 136.6 allowing the method modification. Specific details of the modification need not be provided, but must be documented in the Standard Operating Procedure (SOP) and maintained by the analytical laboratory that performs the analysis.

■ 8. In appendix A to part 136:

■ a. Remove Method 608;

■ b. Add Method 608.3;

■ c. Revise Method 611 section 1.1.;

■ d. Remove Method 624;

■ e. Add Method 624.1;

■ f. Remove Method 625; and

■ g. Add Method 625.1.

The additions and revisions read as follows:

Appendix A to Part 136—Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater

* * * * *

Method 608.3—Organochlorine Pesticides And PCBs By GC/HSD

1. Scope and Application

1.1 This method is for determination of organochlorine pesticides and polychlorinated biphenyls (PCBs) in industrial discharges and other environmental samples by gas chromatography (GC) combined with a halogen-specific detector (HSD; *e.g.*, electron capture, electrolytic conductivity), as provided under 40 CFR 136.1. This revision is based on a previous protocol (Reference 1), on the revision promulgated October 26, 1984, on an inter-laboratory method validation study (Reference 2), and on EPA Method 1656 (Reference 16). The analytes that may be qualitatively and quantitatively determined using this method and their CAS Registry numbers are listed in Table 1.

1.2 This method may be extended to determine the analytes listed in Table 2. However, extraction or gas chromatography challenges for some of these analytes may make quantitative determination difficult.

1.3 When this method is used to analyze unfamiliar samples for an analyte listed in Table 1 or Table 2, analyte identification must be supported by at least one additional

qualitative technique. This method gives analytical conditions for a second GC column that can be used to confirm and quantify measurements. Additionally, Method 625.1 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative confirmation of results for the analytes listed in Tables 1 and 2 using the extract produced by this method, and Method 1699 (Reference 18) provides high resolution GC/MS conditions for qualitative confirmation of results using the original sample. When such methods are used to confirm the identifications of the target analytes, the quantitative results should be derived from the procedure with the calibration range and sensitivity that are most appropriate for the intended application.

1.4 The large number of analytes in Tables 1 and 2 makes testing difficult if all analytes are determined simultaneously. Therefore, it is necessary to determine and perform quality control (QC) tests for the “analytes of interest” only. The analytes of interest are those required to be determined by a regulatory/control authority or in a permit, or by a client. If a list of analytes is not specified, the analytes in Table 1 must be determined, at a minimum, and QC testing must be performed for these analytes. The analytes in Table 1 and some of the analytes in Table 2 have been identified as Toxic Pollutants (40 CFR 401.15), expanded to a list of Priority Pollutants (40 CFR part 423, appendix A).

1.5 In this revision to Method 608, Chlordane has been listed as the alpha- and gamma- isomers in Table 1. Reporting may be by the individual isomers, or as the sum of the concentrations of these isomers, as requested or required by a regulatory/control authority or in a permit. Technical Chlordane is listed in Table 2 and may be used in cases where historical reporting has only been the Technical Chlordane. Toxaphene and the PCBs have been moved from Table 1 to Table 2 (Additional Analytes) to distinguish these analytes from the analytes required in quality control tests (Table 1). QC acceptance criteria for Toxaphene and the PCBs have been retained in Table 4 and may continue to be applied if desired, or if these analytes are requested or required by a regulatory/control authority or in a permit. Method 1668C (Reference 17) may be useful for determination of PCBs as individual chlorinated biphenyl congeners, and Method 1699 (Reference 18) may be useful for determination of the pesticides listed in this method. However, at the time of writing of this revision, Methods 1668C and 1699 had not been approved for use at 40 CFR part 136.

1.6 Method detection limits (MDLs; Reference 3) for the analytes in Tables 1 and some of the analytes in Table 2 are listed in those tables. These MDLs were determined in reagent water (Reference 3). Advances in analytical technology, particularly the use of capillary (open-tubular) columns, allowed laboratories to routinely achieve MDLs for the analytes in this method that are 2–10 times lower than those in the version promulgated in 1984. The MDL for an analyte in a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.6.1 EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described in section 15.6 are focused on such monitoring needs and may not be relevant to other uses of the method.

1.6.2 This method includes “reporting limits” based on EPA’s “minimum level” (ML) concept (see the glossary in section 23). Tables 1 and 2 contain MDL values and ML values for many of the analytes.

1.7 The separatory funnel and continuous liquid-liquid sample extraction and concentration steps in this method are essentially the same as those steps in Methods 606, 609, 611, and 612. Thus, a single sample may be extracted to measure the analytes included in the scope of each of these methods. Samples may also be extracted using a disk-based solid-phase extraction (SPE) procedure developed by the 3M Corporation and approved by EPA as an Alternate Test Procedure (ATP) for wastewater analyses in 1995 (Reference 20).

1.8 This method is performance-based. It may be modified to improve performance (e.g., to overcome interferences or improve the accuracy of results) provided all performance requirements are met.

1.8.1 Examples of allowed method modifications are described at 40 CFR 136.6. Other examples of allowed modifications specific to this method are described in section 8.1.2.

1.8.2 Any modification beyond those expressly permitted at 40 CFR 136.6 or in section 8.1.2 of this method shall be considered a major modification subject to application and approval of an alternate test procedure under 40 CFR 136.4 and 136.5.

1.8.3 For regulatory compliance, any modification must be demonstrated to produce results equivalent or superior to results produced by this method when applied to relevant wastewaters (section 8.1.2).

1.9 This method is restricted to use by or under the supervision of analysts experienced in the use of GC/HSD. The laboratory must demonstrate the ability to generate acceptable results with this method using the procedure in section 8.2.

1.10 Terms and units of measure used in this method are given in the glossary at the end of the method.

2. Summary of Method

2.1 A measured volume of sample, the amount required to meet an MDL or reporting limit (nominally 1–L), is extracted with methylene chloride using a separatory funnel, a continuous liquid/liquid extractor, or disk-based solid-phase extraction equipment. The extract is dried and concentrated for cleanup, if required. After cleanup, or if cleanup is not required, the extract is exchanged into an appropriate solvent and concentrated to the volume necessary to meet the required compliance or detection limit, and analyzed by GC/HSD.

2.2 Qualitative identification of an analyte in the extract is performed using the retention times on dissimilar GC columns. Quantitative analysis is performed using the peak areas or peak heights for the analyte on

the dissimilar columns with either the external or internal standard technique.

2.3 Florisil®, alumina, a C18 solid-phase cleanup, and an elemental sulfur cleanup procedure are provided to aid in elimination of interferences that may be encountered. Other cleanup procedures may be used if demonstrated to be effective for the analytes in a wastewater matrix.

3. Contamination and Interferences

3.1 Solvents, reagents, glassware, and other sample processing lab ware may yield artifacts, elevated baselines, or matrix interferences causing misinterpretation of chromatograms. All materials used in the analysis must be demonstrated free from contamination and interferences by running blanks initially and with each extraction batch (samples started through the extraction process in a given 24-hour period, to a maximum of 20 samples—see Glossary for detailed definition), as described in section 8.5. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, labware is cleaned by extraction or solvent rinse, or baking in a kiln or oven.

3.2 Glassware must be scrupulously cleaned (Reference 4). Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and reagent water. The glassware should then be drained dry, and heated at 400 °C for 15–30 minutes. Some thermally stable materials, such as PCBs, may require higher temperatures and longer baking times for removal. Solvent rinses with pesticide quality acetone, hexane, or other solvents may be substituted for heating. Do not heat volumetric labware above 90 °C. After drying and cooling, store inverted or capped with solvent-rinsed or baked aluminum foil in a clean environment to prevent accumulation of dust or other contaminants.

3.3 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. The phthalate esters generally appear in the chromatogram as large late eluting peaks, especially in the 15 and 50% fractions from Florisil®. Common flexible plastics contain varying amounts of phthalates that may be extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding use of non-fluoropolymer plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination (References 5 and 6). Interferences from phthalate esters can be avoided by using a microcoulometric or electrolytic conductivity detector.

3.4 Matrix interferences may be caused by contaminants co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. Interferences extracted from

samples high in total organic carbon (TOC) may result in elevated baselines, or by enhancing or suppressing a signal at or near the retention time of an analyte of interest. Analyses of the matrix spike and matrix spike duplicate (Section 8.3) may be useful in identifying matrix interferences, and the cleanup procedures in Section 11 may aid in eliminating these interferences. EPA has provided guidance that may aid in overcoming matrix interferences (Reference 7); however, unique samples may require additional cleanup approaches to achieve the MDLs listed in Tables 1 and 2.

4. Safety

4.1 Hazards associated with each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDSs, OSHA, 29 CFR 1910.12009(g)) should also be made available to all personnel involved in sample handling and chemical analysis. Additional references to laboratory safety are available and have been identified (References 8 and 9) for the information of the analyst.

4.2 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic analytes should be prepared in a chemical fume hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

4.3 This method allows the use of hydrogen as a carrier gas in place of helium (section 5.8.2). The laboratory should take the necessary precautions in dealing with hydrogen, and should limit hydrogen flow at the source to prevent buildup of an explosive mixture of hydrogen in air.

5. Apparatus and Materials

Note: Brand names and suppliers are for illustration purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here. Demonstrating that the equipment and supplies used in the laboratory achieve the required performance is the responsibility of the laboratory. Suppliers for equipment and materials in this method may be found through an on-line search. Please do not contact EPA for supplier information.

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—Amber glass bottle large enough to contain the necessary sample volume (nominally 1 L), fitted with a fluoropolymer-lined screw cap. Foil may be substituted for fluoropolymer if the sample is not corrosive. If amber bottles are not available, protect samples from light. Unless pre-cleaned, the bottle and cap liner must be washed, rinsed with acetone or methylene

chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must use a glass or fluoropolymer container and tubing for sample collection. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, rinse the compressible tubing thoroughly with methanol, followed by repeated rinsing with reagent water to minimize the potential for sample contamination. An integrating flow meter is required to collect flow proportional composites. The sample container must be kept refrigerated at $\leq 6^\circ\text{C}$ and protected from light during compositing.

5.2. Lab ware.

5.2.1 Extraction.

5.2.1.1 pH measurement.

5.2.1.1.1 pH meter, with combination glass electrode.

5.2.1.1.2 pH paper, wide range (Hydriion Papers, or equivalent).

5.2.1.2 Separatory funnel—Size appropriate to hold the sample and extraction solvent volumes, equipped with fluoropolymer stopcock.

5.2.1.3 Continuous liquid-liquid extractor—Equipped with fluoropolymer or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, NJ, or equivalent.)

5.2.1.3.1 Round-bottom flask, 500-mL, with heating mantle.

5.2.1.3.2 Condenser, Graham, to fit extractor.

5.2.1.4 Solid-phase extractor—90-mm filter apparatus (Figure 2) or multi-position manifold.

Note: The approved ATP for solid-phase extraction is limited to disk-based extraction media and associated peripheral equipment.

5.2.1.4.1 Vacuum system—Capable of achieving 0.1 bar (25 inch) Hg (house vacuum, vacuum pump, or water aspirator), equipped with shutoff valve and vacuum gauge.

5.2.1.4.2 Vacuum trap—Made from 500-mL sidearm flask fitted with single-hole rubber stopper and glass tubing.

5.2.2 Filtration.

5.2.2.1 Glass powder funnel, 125- to 250-mL.

5.2.2.2 Filter paper for above, Whatman 41, or equivalent.

5.2.2.3 Prefiltering aids—90-mm 1- μm glass fiber filter or Empore® Filter Aid 400.

5.2.3 Drying column.

5.2.3.1 Chromatographic column—Approximately 400 mm long x 15 mm ID, with fluoropolymer stopcock and coarse frit filter disc (Kontes or equivalent).

5.2.3.2 Glass wool—Pyrex, extracted with methylene chloride or baked at 450°C for 1 hour minimum.

5.2.4 Column for Florisil® or alumina cleanup—Approximately 300 mm long x 10 mm ID, with fluoropolymer stopcock. (This column is not required if cartridges containing Florisil® are used.)

5.2.5 Concentration/evaporation.

Note: Use of a solvent recovery system with the K-D or other solvent evaporation apparatus is strongly recommended.

5.2.5.1 Kuderna-Danish concentrator.

5.2.5.1.1 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes or equivalent). Calibration must be checked at the volumes employed for extract volume measurement. A ground-glass stopper is used to prevent evaporation of extracts.

5.2.5.1.2 Evaporative flask, Kuderna-Danish—500-mL (Kontes or equivalent). Attach to concentrator tube with connectors.

5.2.5.1.3 Snyder column, Kuderna/Danish—Three-ball macro (Kontes or equivalent).

5.2.5.1.4 Snyder column—Two-ball micro (Kontes or equivalent).

5.2.5.1.5 Water bath—Heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$), installed in a hood using appropriate engineering controls to limit exposure to solvent vapors.

5.2.5.2 Nitrogen evaporation device—Equipped with heated bath that can be maintained at an appropriate temperature for the solvent and analytes. (N-Evap, Organomation Associates, Inc., or equivalent).

5.2.5.3 Rotary evaporator—Buchi/Brinkman-American Scientific or equivalent, equipped with a variable temperature water bath, vacuum source with shutoff valve at the evaporator, and vacuum gauge.

5.2.5.3.1 A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.

5.2.5.3.2 Round-bottom flask—100-mL and 500-mL or larger, with ground-glass fitting compatible with the rotary evaporator

Note: This equipment is used to prepare copper foil or copper powder for removing sulfur from sample extracts (see Section 6.7.4).

5.2.5.4 Automated concentrator—Equipped with glassware sufficient to concentrate 3–400 mL extract to a final volume of 1–10 mL under controlled conditions of temperature and nitrogen flow (Turbovap, or equivalent). Follow manufacturer's directions and requirements.

5.2.5.5 Boiling chips—Glass, silicon carbide, or equivalent, approximately 10/40 mesh. Heat at 400°C for 30 minutes, or solvent rinse or Soxhlet extract with methylene chloride.

5.2.6 Solid-phase extraction disks—90-mm extraction disks containing 2 g of 8- μm octadecyl (C18) bonded silica uniformly enmeshed in a matrix of inert PTFE fibrils (3M Empore® or equivalent). The disks should not contain any organic compounds, either from the PTFE or the bonded silica, which will leach into the methylene chloride eluant. One liter of reagent water should pass through the disks in 2–5 minutes, using a vacuum of at least 25 inches of mercury.

Note: Extraction disks from other manufacturers may be used in this procedure, provided that they use the same solid-phase materials (*i.e.*, octadecyl bonded silica). Disks of other diameters also may be used, but may adversely affect the flow rate of the sample through the disk.

5.3 Vials.

5.3.1 Extract storage—10- to 15-mL, amber glass, with fluoropolymer-lined screw cap.

5.3.2 GC autosampler—1- to 5-mL, amber glass, with fluoropolymer-lined screw- or crimp-cap, to fit GC autosampler.

5.4 Balances.

5.4.1 Analytical—Capable of accurately weighing 0.1 mg.

5.4.2 Top loading—Capable of weighing 10 mg.

5.5 Sample cleanup.

5.5.1 Oven—For baking and storage of adsorbents, capable of maintaining a constant temperature (± 5 °C) in the range of 105–250 °C.

5.5.2 Muffle furnace—Capable of cleaning glassware or baking sodium sulfate in the range of 400–450 °C.

5.5.3 Vacuum system and cartridges for solid-phase cleanup (see Section 11.2).

5.5.3.1 Vacuum system—Capable of achieving 0.1 bar (25 in.) Hg (house vacuum, vacuum pump, or water aspirator), equipped with shutoff valve and vacuum gauge.

5.5.3.2 VacElute Manifold (Analytichem International, or equivalent).

5.5.3.3 Vacuum trap—Made from 500-mL sidearm flask fitted with single-hole rubber stopper and glass tubing.

5.5.3.4 Rack for holding 50-mL volumetric flasks in the manifold.

5.5.3.5 Cartridge—Mega Bond Elute, Non-polar, C18 Octadecyl, 10 g/60 mL (Analytichem International or equivalent), used for solid-phase cleanup of sample extracts (see Section 11.2).

5.5.4 Sulfur removal tube—40- to 50-mL bottle, test tube, or Erlenmeyer flask with fluoropolymer-lined screw cap.

5.6 Centrifuge apparatus.

5.6.1 Centrifuge—Capable of rotating 500-mL centrifuge bottles or 15-mL centrifuge tubes at 5,000 rpm minimum.

5.6.2 Centrifuge bottle—500-mL, with screw cap, to fit centrifuge.

5.6.3 Centrifuge tube—15-mL, with screw cap, to fit centrifuge.

5.7 Miscellaneous lab ware—Graduated cylinders, pipettes, beakers, volumetric flasks, vials, syringes, and other lab ware necessary to support the operations in this method.

5.8 Gas chromatograph—Dual-column with simultaneous split/splitless, temperature programmable split/splitless (PTV), or on-column injection; temperature program with isothermal holds, and all required accessories including syringes, analytical columns, gases, and detectors. An autosampler is highly recommended because it injects volumes more reproducibly than manual injection techniques. Alternatively, two separate single-column gas chromatographic systems may be employed.

5.8.1 Example columns and operating conditions.

5.8.1.1 DB-608 (or equivalent), 30-m long \times 0.53-mm ID fused-silica capillary, 0.83- μ m film thickness.

5.8.1.2 DB-1701 (or equivalent), 30-m long \times 0.53-mm ID fused-silica capillary, 1.0- μ m film thickness.

5.8.1.3 Suggested operating conditions used to meet the retention times shown in Table 3 are:

(a) Carrier gas flow rate: Approximately 7 mL/min,

(b) Initial temperature: 150 °C for 0.5 minute,

(c) Temperature program: 150–270 °C at 5 °C/min, and

(d) Final temperature: 270 °C, until *trans*-Permethrin elutes.

Note: Other columns, internal diameters, film thicknesses, and operating conditions may be used, provided that the performance requirements in this method are met. However, the column pair chosen must have dissimilar phases/chemical properties in order to separate the compounds of interest in different retention time order. Columns that only differ in the length, ID, or film thickness, but use the same stationary phase do not qualify as “dissimilar.”

5.8.2 Carrier gas—Helium or hydrogen. Data in the tables in this method were obtained using helium carrier gas. If hydrogen is used, analytical conditions may need to be adjusted for optimum performance, and calibration and all QC tests must be performed with hydrogen carrier gas. See Section 4.3 for precautions regarding the use of hydrogen as a carrier gas.

5.8.3 Detector—Halogen-specific detector (electron capture detector [ECD], electrolytic conductivity detector [ELCD], or equivalent). The ECD has proven effective in the analysis of wastewaters for the analytes listed in Tables 1 and 2, and was used to develop the method performance data in Section 17 and Tables 4 and 5.

5.8.4 Data system—A computer system must be interfaced to the GC that allows continuous acquisition and storage of data from the detectors throughout the chromatographic program. The computer must have software that allows searching GC data for specific analytes, and for plotting responses versus time. Software must also be available that allows integrating peak areas or peak heights in selected retention time windows and calculating concentrations of the analytes.

6. Reagents and Standards

6.1 pH adjustment.

6.1.1 Sodium hydroxide solutions.

6.1.1.1 Concentrated (10 M)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.1.1.2 Dilute (1 M)—Dissolve 40 g NaOH in 1 L of reagent water.

6.1.2 Sulfuric acid (1+1)—Slowly add 50 mL of H₂SO₄ (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.1.3 Hydrochloric acid—Reagent grade, 6 N.

6.2 Sodium thiosulfate—(ACS) granular.

6.3 Sodium sulfate—Sodium sulfate, reagent grade, granular anhydrous (Baker or equivalent), rinsed with methylene chloride, baked in a shallow tray at 450 °C for 1 hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw cap which prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and

baking at a lower temperature may produce sodium sulfate suitable for use.

6.4 Reagent water—Reagent water is defined as water in which the analytes of interest and interfering compounds are not observed at the MDLs of the analytes in this method.

6.5 Solvents—Methylene chloride, acetone, methanol, hexane, acetonitrile, and isooctane, high purity pesticide quality, or equivalent, demonstrated to be free of the analytes and interferences (section 3). Purification of solvents by distillation in all-glass systems may be required.

Note: The standards and final sample extracts must be prepared in the same final solvent.

6.6 Ethyl ether—Nanograde, redistilled in glass if necessary. Ethyl ether must be shown to be free of peroxides before use, as indicated by EM Laboratories Quant test strips (available from Scientific Products Co. and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips. After removal of peroxides, add 20 mL of ethyl alcohol preservative to each liter of ether.

6.7 Materials for sample cleanup.

6.7.1 Florisil®—PR grade (60/100 mesh), activated at 650–700 °C, stored in the dark in a glass container with fluoropolymer-lined screw cap. Activate each batch immediately prior to use for 16 hours minimum at 130 °C in a foil-covered glass container and allow to cool. Alternatively, 500 mg cartridges (J.T. Baker, or equivalent) may be used.

6.7.1.1 Cartridge certification—Each cartridge lot must be certified to ensure recovery of the analytes of interest and removal of 2,4,6-trichlorophenol. To make the test mixture, add the trichlorophenol solution (section 6.7.1.3) to the same standard used to prepare the Quality Control Check Sample (section 6.8.3). Transfer the mixture to the column and dry the column. Pre-elute with three 10-mL portions of elution solvent, drying the column between elutions. Elute the cartridge with 10 mL each of methanol and water, as in section 11.2.3.3.

6.7.1.2 Concentrate the eluant to per section 10.3.3, exchange to isooctane or hexane per section 10.3.3, and inject 1.0 μ L of the concentrated eluant into the GC using the procedure in section 12. The recovery of all analytes (including the unresolved GC peaks) shall be within the ranges for calibration verification (section 13.6 and Table 4), the recovery of trichlorophenol shall be less than 5%, and no peaks interfering with the target analytes shall be detected. Otherwise the Florisil cartridge is not performing properly and the cartridge lot shall be rejected.

6.7.1.3 Florisil cartridge calibration solution—2,4,6-Trichlorophenol, 0.1 μ g/mL in acetone.

6.7.2 SPE elution solvent—Methylene chloride:acetonitrile:hexane (50:3:47).

6.7.3 Alumina, neutral, Brockman Activity I, 80–200 mesh (Fisher Scientific certified, or equivalent). Heat in a glass bottle for 16 hours at 400 to 450 °C. Seal and cool to room temperature. Add 7% (w/w) reagent water and mix for 10 to 12 hours. Keep bottle tightly sealed.

6.7.4 Sulfur removal.

6.7.4.1 Copper foil or powder—Fisher, Alfa Aesar, or equivalent. Cut copper foil into approximately 1-cm squares. Copper must be activated before it may be used, as described below.

6.7.4.1.1 Place the quantity of copper needed for sulfur removal (section 11.5.1.3) in a ground-glass-stoppered Erlenmeyer flask or bottle. Cover the foil or powder with methanol.

6.7.4.1.2 Add HCl dropwise (0.5–1.0 mL) while swirling, until the copper brightens.

6.7.4.1.3 Pour off the methanol/HCl and rinse 3 times with reagent water to remove all traces of acid, then 3 times with acetone, then 3 times with hexane.

6.7.4.1.4 For copper foil, cover with hexane after the final rinse. Store in a stoppered flask under nitrogen until used. For the powder, dry on a rotary evaporator. Store in a stoppered flask under nitrogen until used. Inspect the copper foil or powder before each use. It must have a bright, non-oxidized appearance to be effective. Copper foil or powder that has oxidized may be reactivated using the procedure described above.

6.7.4.2 Tetrabutylammonium sulfite (TBA sulfite)—Prepare as described below.

6.7.4.2.1 Tetrabutylammonium hydrogen sulfate, $[\text{CH}_3(\text{CH}_2)_3]_4\text{NHSO}_4$.

6.7.4.2.2 Sodium sulfite, Na_2SO_3 .

6.7.4.2.3 Dissolve approximately 3 g tetrabutylammonium hydrogen sulfate in 100 mL of reagent water in an amber bottle with fluoropolymer-lined screw cap. Extract with three 20-mL portions of hexane and discard the hexane extracts.

6.7.4.2.4 Add 25 g sodium sulfite to produce a saturated solution. Store at room temperature. Replace after 1 month.

6.7.5 Sodium chloride—Reagent grade, prepare at 5% (w/v) solution in reagent water.

6.8 Stock standard solutions—Stock standard solutions may be prepared from pure materials, or purchased as certified solutions. Traceability must be to the National Institute of Standards and Technology (NIST) or other national or international standard, when available. Stock solution concentrations alternative to those below may be used. Because of the toxicity of some of the compounds, primary dilutions should be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations of neat materials are handled. The following procedure may be used to prepare standards from neat materials.

6.8.1 Accurately weigh about 0.0100 g of pure material in a 10-mL volumetric flask. Dilute to volume in pesticide quality hexane, isooctane, or other suitable solvent. Larger volumes may be used at the convenience of the laboratory. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.8.1.1 Unless stated otherwise in this method, store non-aqueous standards in

fluoropolymer-lined screw-cap, or heat-sealed, glass containers, in the dark at -20 to -10°C . Store aqueous standards; e.g., the aqueous LCS (section 8.4), in the dark at $\leq 6^\circ\text{C}$, but do not freeze.

6.8.1.2 Standards prepared by the laboratory may be stored for up to one year, except when comparison with QC check standards indicates that a standard has degraded or become more concentrated due to evaporation, or unless the laboratory has data on file to prove stability for a longer period. Commercially prepared standards may be stored until the expiration date provided by the vendor, except when comparison with QC check standards indicates that a standard has degraded or become more concentrated due to evaporation, or unless the laboratory has data from the vendor on file to prove stability for a longer period.

6.8.2 Calibration solutions—It is necessary to prepare calibration solutions for the analytes of interest (section 1.4) only using an appropriate solvent (isooctane or hexane may be used). Whatever solvent is used, both the calibration standards and the final sample extracts must use the same solvent. Other analytes may be included as desired.

6.8.2.1 Prepare calibration standards for the single-component analytes of interest and surrogates at a minimum of three concentration levels (five are suggested) by adding appropriate volumes of one or more stock standards to volumetric flasks. One of the calibration standards should be at a concentration at or below the ML specified in Table 1, or 2, or as specified by a regulatory/control authority or in a permit. The ML value may be rounded to a whole number that is more convenient for preparing the standard, but must not exceed the ML value listed in Tables 1 or 2 for those analytes which list ML values. Alternatively, the laboratory may establish an ML for each analyte based on the concentration of the lowest calibration standard in a series of standards produced by the laboratory or obtained from a commercial vendor, again, provided that the ML does not exceed the ML in Table 1 and 2, and provided that the resulting calibration meets the acceptance criteria in section 7.5.2 based on the RSD, RSE, or R^2 .

(a) The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC system. A minimum of six concentration levels is required for a second order, non-linear (e.g., quadratic; $ax^2 + bx + c = 0$) calibration (section 7.5.2 or 7.6.2). Calibrations higher than second order are not allowed. A separate standard near the MDL may be analyzed as a check on sensitivity, but should not be included in the linearity assessment. The solvent for the standards must match the final solvent for the sample extracts (e.g., isooctane or hexane).

Note: The option for non-linear calibration may be necessary to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation or to avoid proper instrument maintenance.

(b) Given the number of analytes included in this method, it is highly likely that some will coelute on one or both of the GC columns used for the analysis. Divide the analytes into two or more groups and prepare separate calibration standards for each group, at multiple concentrations (e.g., a five-point calibration will require ten solutions to cover two groups of analytes). Table 7 provides information on dividing the target analytes into separate calibration mixtures that should minimize or eliminate co-elutions. This table is provided solely as guidance, based on the GC columns suggested in this method. If an analyte listed in Table 7 is not an analyte of interest in a given laboratory setting, then it need not be included in a calibration mixture.

Note: Many commercially available standards are divided into separate mixtures to address this issue.

(c) If co-elutions occur in analysis of a sample, a co-elution on one column is acceptable so long as effective separation of the co-eluting compounds can be achieved on the second column.

6.8.2.2 Multi-component analytes (e.g., PCBs as Aroclors, and Toxaphene).

6.8.2.2.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at three to five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing multi-point initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Therefore, prepare a minimum of three calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

6.8.2.2.2 Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards described in Section 6.8.2.2.1 have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors also may be used to determine the calibration factor for each Aroclor. Prepare a standard for each of the other Aroclors. The concentrations should generally correspond to the mid-point of the linear range of the detector, but lower concentrations may be employed at the discretion of the analyst based on project requirements.

6.8.2.2.3 For Toxaphene, prepare a minimum of three calibration standards containing Toxaphene by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in

real samples and should bracket the linear range of the detector.

6.8.3 Quality Control (QC) Check Sample Concentrate—Prepare one or more mid-level standard mixtures (concentrates) in acetone (or other water miscible solvent). The concentrate is used as the spiking solution with which to prepare the Demonstration of Capabilities (DOC) samples, the Laboratory Control Sample (LCS), and Matrix Spike (MS) and Matrix Spike Duplicate (MSD) samples described in section 8. If prepared by the laboratory (as opposed to purchasing it from a commercial supplier), the concentrate must be prepared independently from the standards used for calibration, but may be prepared from the same source as the second-source standard used for calibration verification (section 7.7). Regardless of the source, the concentrate must be in a water-miscible solvent, as noted above. The concentrate is used to prepare the DOC and LCS (sections 8.2.1 and 8.4) and MS/MSD samples (section 8.3). Depending on the analytes of interest for a given sample (see Section 1.4), multiple solutions and multiple LCS or MS/MSD samples may be required to account for co-eluting analytes. However, a co-elution on one column is acceptable so long as effective separation of the co-eluting compounds can be achieved on the second column. In addition, the concentrations of the MS/MSD samples should reflect any relevant compliance limits for the analytes of interest, as described in section 8.3.1. If a custom spiking solution is required for a specific discharge (section 8.3.1), prepare it separately from the DOC and LCS solution.

Note: Some commercially available standards are divided into separate mixtures to address the co-elution issue.

6.8.4 Calibration Verification Standards—In order to verify the results of the initial calibration standards, prepare one or more mid-level standard mixtures in isooctane or hexane, using standards obtained from a second source (different manufacturer or different certified lot from the calibration standards). These standards will be analyzed to verify the accuracy of the calibration (sections 7.7 and 13.6.2). As with the QC sample concentrate in section 6.8.3, multiple solutions may be required to address co-elutions among all of the analytes.

6.8.5 Internal standard solution—If the internal standard calibration technique is to be used, prepare pentachloronitrobenzene (PCNB) at a concentration of 10 µg/mL in ethyl acetate. Alternative and multiple internal standards; *e.g.*, tetrachloro-*m*-xylene, 4,4'-dibromobiphenyl, and/or decachlorobiphenyl may be used provided that the laboratory performs all QC tests and meets all QC acceptance criteria with the alternative or additional internal standard(s) as an integral part of this method.

6.8.6 Surrogate solution—Prepare a solution containing one or more surrogates at a concentration of 2 µg/mL in acetone. Potential surrogates include: dibutyl chlorendate (DBC), tetrachloro-*m*-xylene (TCMX), 4,4'-dibromobiphenyl, or decachlorobiphenyl. Alternative surrogates and concentrations may be used, provided the laboratory performs all QC tests and

meets all QC acceptance criteria with the alternative surrogate(s) as an integral part of this method. If the internal standard calibration technique is used, do not use the internal standard as a surrogate.

6.8.7 DDT and endrin decomposition (breakdown) solution—Prepare a solution containing endrin at a concentration of 50 ng/mL and 4,4'-DDT at a concentration of 100 ng/mL, in isooctane or hexane. A 1-µL injection of this standard will contain 50 picograms (pg) of endrin and 100 pg of DDT. The concentration of the solution may be adjusted by the laboratory to accommodate other injection volumes such that the same masses of the two analytes are introduced into the instrument.

7. Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those in Section 5.8.1 and Footnote 2 to Table 3. Alternative temperature program and flow rate conditions may be used. The system may be calibrated using the external standard technique (section 7.5) or the internal standard technique (section 7.6). It is necessary to calibrate the system for the analytes of interest (section 1.4) only.

7.2 Separately inject the mid-level calibration standard for each calibration mixture. Store the retention time on each GC column.

7.3 Injection of calibration solutions—Inject a constant volume in the range of 0.5 to 2.0 µL of each calibration solution into the GC column/detector pairs. An alternative volume (see Section 12.3) may be used provided all requirements in this method are met. Beginning with the lowest level mixture and proceeding to the highest level mixture may limit the risk of carryover from one standard to the next, but other sequences may be used. An instrument blank should be analyzed after the highest standard to demonstrate that there is no carry-over within the system for this calibration range.

7.4 For each analyte, compute, record, and store, as a function of the concentration injected, the retention time and peak area on each column/detector system. If multi-component analytes are to be analyzed, store the retention time and peak area for the three to five exclusive (unique large) peaks for each PCB or technical chlordane. Use four to six peaks for toxaphene.

7.5 External standard calibration.

7.5.1 From the calibration data (Section 7.4), calculate the calibration factor (CF) for each analyte at each concentration according to the following equation:

$$CF = \frac{A_s}{C_s}$$

Where:

C_s = Concentration of the analyte in the standard (ng/mL)

A_s = Peak height or area

For multi-component analytes, choose a series of characteristic peaks for each analyte (3 to 5 for each Aroclor, 4 to 6 for toxaphene) and calculate individual calibration factors for each peak. Alternatively, for toxaphene, sum the areas of all of the peaks in the standard chromatogram and use the summed

area to determine the calibration factor. (If this alternative is used, the same approach must be used to quantitate the analyte in the samples.)

7.5.2 Calculate the mean (average) and relative standard deviation (RSD) of the calibration factors. If the RSD is less than 20%, linearity through the origin can be assumed and the average CF can be used for calculations. Alternatively, the results can be used to fit a linear or quadratic regression of response, A_s , vs. concentration C_s . If used, the regression must be weighted inversely proportional to concentration. The coefficient of determination (R^2) of the weighted regression must be greater than 0.920. Alternatively, the relative standard error (Reference 10) may be used as an acceptance criterion. As with the RSD, the RSE must be less than 20%. If an RSE less than 20% cannot be achieved for a quadratic regression, system performance is unacceptable and the system must be adjusted and re-calibrated.

Note: Regression calculations are not included in this method because the calculations are cumbersome and because many GC/ECD data systems allow selection of weighted regression for calibration and calculation of analyte concentrations.

7.6 Internal standard calibration.

7.6.1 From the calibration data (Section 7.4), calculate the response factor (RF) for each analyte at each concentration according to the following equation:

$$RF = \frac{(A_s \times C_{is})}{(A_{is} \times C_s)}$$

Where:

A_s = Response for the analyte to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard (ng/mL)

C_s = Concentration of the analyte to be measured (ng/mL).

7.6.2 Calculate the mean (average) and relative standard deviation (RSD) of the response factors. If the RSD is less than 15%, linearity through the origin can be assumed and the average RF can be used for calculations. Alternatively, the results can be used to prepare a calibration curve of response ratios, A_s/A_{is} , vs. concentration ratios, C_s/C_{is} , for the analyte. A minimum of six concentration levels is required for a non-linear (*e.g.*, quadratic) regression. If used, the regression must be weighted inversely proportional to concentration, and the coefficient of determination of the weighted regression must be greater than 0.920.

Alternatively, the relative standard error (Reference 10) may be used as an acceptance criterion. As with the RSD, the RSE must be less than 15%. If an RSE less than 15% cannot be achieved for a quadratic regression, system performance is unacceptable and the system must be adjusted and re-calibrated.

7.7 The working calibration curve, CF, or RF must be verified immediately after calibration and at the beginning and end of each 24-hour shift by the analysis of a mid-level calibration standard. The calibration verification standard(s) must be obtained from a second manufacturer or a manufacturer's batch prepared

independently from the batch used for calibration (Section 6.8.4). Requirements for calibration verification are given in Section 13.6 and Table 4. Alternatively, calibration verification may be performed after a set number of injections (e.g., every 20 injections), to include injection of extracts of field samples, QC samples, instrument blanks, etc. (i.e., it is based on the number of injections performed, not sample extracts). The time for the injections may not exceed 24 hours.

Note: The 24-hour shift begins after analysis of the combined QC standard (calibration verification) and ends 24 hours later. The ending calibration verification standard is run immediately after the last sample run during the 24-hour shift, so the beginning and ending calibration verifications are outside of the 24-hour shift. If calibration verification is based on the number of injections instead of time, then the ending verification standard for one group of injections may be used as the beginning verification for the next group of injections.

7.8 Florisil® calibration—The column cleanup procedure in Section 11.3 utilizes Florisil column chromatography. Florisil® from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil® which is used, use of the lauric acid value (Reference 11) is suggested. The referenced procedure determines the adsorption to a hexane solution of lauric acid (mg) per g of Florisil®. The amount of Florisil® to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g. If cartridges containing Florisil® are used, then this step is not necessary.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analysis of spiked samples and blanks to evaluate and document data quality. The laboratory must maintain records to document the quality of data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet performance requirements of this method. A quality control check standard (LCS, section 8.4) must be prepared and analyzed with each batch of samples to confirm that the measurements were performed in an in-control mode of operation. A laboratory may develop its own performance criteria (as QC acceptance criteria), provided such criteria are as or more restrictive than the criteria in this method.

8.1.1 The laboratory must make an initial demonstration of the capability (IDC) to generate acceptable precision and recovery with this method. This demonstration is detailed in Section 8.2. On a continuing basis, the laboratory must repeat demonstration of capability (DOC) at least annually.

8.1.2 In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory

is permitted certain options (section 1.8 and 40 CFR 136.6(b) [Reference 12]) to improve separations or lower the costs of measurements. These options may include alternative extraction (e.g., other solid-phase extraction materials and formats), concentration, and cleanup procedures, and changes in GC columns (Reference 12). Alternative determinative techniques, such as the substitution of spectroscopic or immunoassay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, that technique must have a specificity equal to or greater than the specificity of the techniques in this method for the analytes of interest. The laboratory is also encouraged to participate in performance evaluation studies (see section 8.8).

8.1.2.1 Each time a modification listed above is made to this method, the laboratory is required to repeat the procedure in section 8.2. If the detection limit of the method will be affected by the change, the laboratory is required to demonstrate that the MDLs (40 CFR part 136, appendix B) are lower than one-third the regulatory compliance limit or as low as the MDLs in this method, whichever are greater. If calibration will be affected by the change, the instrument must be recalibrated per section 7. Once the modification is demonstrated to produce results equivalent or superior to results produced by this method as written, that modification may be used routinely thereafter, so long as the other requirements in this method are met (e.g., matrix spike/matrix spike duplicate recovery and relative percent difference).

8.1.2.1.1 If an allowed method modification, is to be applied to a specific discharge, the laboratory must prepare and analyze matrix spike/matrix spike duplicate (MS/MSD) samples (section 8.3) and LCS samples (section 8.4). The laboratory must include surrogates (Section 8.7) in each of the samples. The MS/MSD and LCS samples must be fortified with the analytes of interest (section 1.4). If the modification is for nationwide use, MS/MSD samples must be prepared from a minimum of nine different discharges (See section 8.1.2.1.2), and all QC acceptance criteria in this method must be met. This evaluation only needs to be performed once other than for the routine QC required by this method (for example it could be performed by the vendor of an alternative material) but any laboratory using that specific material must have the results of the study available. This includes a full data package with the raw data that will allow an independent reviewer to verify each determination and calculation performed by the laboratory (see section 8.1.2.2.5, items (a)–(q)).

8.1.2.1.2 Sample matrices on which MS/MSD tests must be performed for nationwide use of an allowed modification:

- (a) Effluent from a publicly owned treatment works (POTW).
- (b) ASTM D5905 Standard Specification for Substitute Wastewater.
- (c) Sewage sludge, if sewage sludge will be in the permit.

(d) ASTM D1141 Standard Specification for Substitute Ocean Water, if ocean water will be in the permit.

(e) Untreated and treated wastewaters up to a total of nine matrix types (see <https://www.epa.gov/eg/industrial-effluent-guidelines> for a list of industrial categories with existing effluent guidelines).

(i) At least one of the above wastewater matrix types must have at least one of the following characteristics:

- (A) Total suspended solids greater than 40 mg/L.
- (B) Total dissolved solids greater than 100 mg/L.
- (C) Oil and grease greater than 20 mg/L.
- (D) NaCl greater than 120 mg/L.
- (E) CaCO₃ greater than 140 mg/L.

(ii) The interim acceptance criteria for MS, MSD recoveries that do not have recovery limits in Table 4 or developed in section 8.3.3, and for surrogates that do not have recovery limits developed in section 8.6, must be no wider than 60–140%, and the relative percent difference (RPD) of the concentrations in the MS and MSD that do not have RPD limits in Table 4 or developed in section 8.3.3, must be less than 30%. Alternatively, the laboratory may use the laboratory's in-house limits if they are tighter.

(f) A proficiency testing (PT) sample from a recognized provider, in addition to tests of the nine matrices (section 8.1.2.1.1).

8.1.2.2 The laboratory must maintain records of modifications made to this method. These records include the following, at a minimum:

8.1.2.2.1 The names, titles, and business street addresses, telephone numbers, and email addresses, of the analyst(s) that performed the analyses and modification, and of the quality control officer that witnessed and will verify the analyses and modifications.

8.1.2.2.2 A list of analytes, by name and CAS Registry number.

8.1.2.2.3 A narrative stating reason(s) for the modifications.

8.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

- (a) Calibration (section 7).
- (b) Calibration verification (section 13.6).
- (c) Initial demonstration of capability (section 8.2).
- (d) Analysis of blanks (section 8.5).
- (e) Matrix spike/matrix spike duplicate analysis (section 8.3).
- (f) Laboratory control sample analysis (section 8.4).

8.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

- (a) Sample numbers and other identifiers.
- (b) Extraction dates.
- (c) Analysis dates and times.
- (d) Analysis sequence/run chronology.
- (e) Sample weight or volume (section 10).
- (f) Extract volume prior to each cleanup step (sections 10 and 11).
- (g) Extract volume after each cleanup step (section 11).
- (h) Final extract volume prior to injection (sections 10 and 12).

- (i) Injection volume (sections 12.3 and 13.2).
- (j) Sample or extract dilution (section 15.4).
- (k) Instrument and operating conditions.
- (l) Column (dimensions, material, etc.).
- (m) Operating conditions (temperatures, flow rates, etc.).
- (n) Detector (type, operating conditions, etc.).
- (o) Chromatograms and other recordings of raw data.
- (p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.
- (q) A written Standard Operating Procedure (SOP).

8.1.2.2.6 Each individual laboratory wishing to use a given modification must perform the start-up tests in section 8.1.2 (e.g., DOC, MDL), with the modification as an integral part of this method prior to applying the modification to specific discharges. Results of the DOC must meet the QC acceptance criteria in Table 5 for the analytes of interest (section 1.4), and the MDLs must be equal to or lower than the MDLs in Tables 1 and 2 for the analytes of interest.

8.1.3 Before analyzing samples, the laboratory must analyze a blank to demonstrate that interferences from the analytical system, lab ware, and reagents, are under control. Each time a batch of samples is extracted or reagents are changed, a blank must be extracted and analyzed as a safeguard against laboratory contamination. Requirements for the blank are given in section 8.5.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze samples to monitor and evaluate method and laboratory performance on the sample matrix. The procedure for spiking and analysis is given in section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through analysis of a quality control check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) that the measurement system is in control. This procedure is described in Section 8.4.

8.1.6 The laboratory should maintain performance records to document the quality of data that is generated. This procedure is given in section 8.7.

8.1.7 The large number of analytes tested in performance tests in this method present a substantial probability that one or more will fail acceptance criteria when all analytes are tested simultaneously, and a re-test (reanalysis) is allowed if this situation should occur. If, however, continued re-testing results in further repeated failures, the laboratory should document the failures and either avoid reporting results for the analytes that failed or report the problem and failures with the data. A QC failure does not relieve a discharger or permittee of reporting timely results.

8.2 Demonstration of capability (DOC)—To establish the ability to generate acceptable recovery and precision, the laboratory must perform the DOC in sections 8.2.1 through 8.2.6 for the analytes of interest initially and in an on-going manner at least annually. The laboratory must also establish MDLs for the analytes of interest using the MDL procedure

at 40 CFR part 136, appendix B. The laboratory's MDLs must be equal to or lower than those listed in Tables 1 or 2, or lower than one-third the regulatory compliance limit, whichever is greater. For MDLs not listed in Tables 1 or 2, the laboratory must determine the MDLs using the MDL procedure at 40 CFR part 136, appendix B under the same conditions used to determine the MDLs for the analytes listed in Tables 1 and 2. When analyzing the PCBs as Aroclors, it is only necessary to establish an MDL for one of the multi-component analytes (e.g., PCB 1254), or the mixture of Aroclors 1016 and 1260 may be used to establish MDLs for all of the Aroclors. Similarly, MDLs for other multi-component analytes (e.g., Chlordanes) may be determined using only one of the major components. All procedures used in the analysis, including cleanup procedures, must be included in the DOC.

8.2.1 For the DOC, a QC check sample concentrate containing each analyte of interest (section 1.4) is prepared in a water-miscible solvent using the solution in section 6.8.3.

Note: QC check sample concentrates are no longer available from EPA.

8.2.2 Using a pipet or syringe, prepare four QC check samples by adding an appropriate volume of the concentrate and of the surrogate(s) to each of four 1-L aliquots of reagent water. Swirl or stir to mix.

8.2.3 Extract and analyze the well-mixed QC check samples according to the method beginning in section 10.

8.2.4 Calculate the average percent recovery (\bar{X}) and the standard deviation (s) of the percent recovery for each analyte using the four results.

8.2.5 For each analyte, compare s and \bar{X} with the corresponding acceptance criteria for precision and recovery in Table 4. For analytes in Table 2 that are not listed in Table 4, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13). If s and \bar{X} for all analytes of interest meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples can begin. If any individual s exceeds the precision limit or any individual \bar{X} falls outside the range for recovery, system performance is unacceptable for that analyte.

Note: The large number of analytes in Tables 1 and 2 present a substantial probability that one or more will fail at least one of the acceptance criteria when many or all analytes are determined simultaneously.

8.2.6 When one or more of the analytes tested fail at least one of the acceptance criteria, repeat the test for only the analytes that failed. If results for these analytes pass, system performance is acceptable and analysis of samples and blanks may proceed. If one or more of the analytes again fail, system performance is unacceptable for the analytes that failed the acceptance criteria. Correct the problem and repeat the test (section 8.2). See section 8.1.7 for disposition of repeated failures.

Note: To maintain the validity of the test and re-test, system maintenance and/or

adjustment is not permitted between this pair of tests.

8.3 Matrix spike and matrix spike duplicate (MS/MSD)—The purpose of the MS/MSD requirement is to provide data that demonstrate the effectiveness of the method as applied to the samples in question by a given laboratory, and both the data user (discharger, permittee, regulated entity, regulatory/control authority, customer, other) and the laboratory share responsibility for provision of such data. The data user should identify the sample and the analytes of interest (section 1.4) to be spiked and provide sufficient sample volume to perform MS/MSD analyses. The laboratory must, on an ongoing basis, spike at least 5% of the samples in duplicate from each discharge being monitored to assess accuracy (recovery and precision). If direction cannot be obtained from the data user, the laboratory must spike at least one sample in duplicate per extraction batch of up to 20 samples with the analytes in Table 1. Spiked sample results should be reported only to the data user whose sample was spiked, or as requested or required by a regulatory/control authority, or in a permit.

8.3.1. If, as in compliance monitoring, the concentration of a specific analyte will be checked against a regulatory concentration limit, the concentration of the spike should be at that limit; otherwise, the concentration of the spike should be one to five times higher than the background concentration determined in section 8.3.2, at or near the midpoint of the calibration range, or at the concentration in the LCS (section 8.4) whichever concentration would be larger. When no information is available, the midpoint of the calibration may be used.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of the each analyte of interest. If necessary to meet the requirement in section 8.3.1, prepare a new check sample concentrate (section 8.2.1) appropriate for the background concentration. Spike and analyze two additional sample aliquots of the same volume as the original sample, and determine the concentrations after spiking (A_1 and A_2) of each analyte. Calculate the percent recoveries (P_1 and P_2) as:

$$P_x = \frac{A_x - B}{T} \times 100$$

where T is the known true value of the spike.

Also calculate the relative percent difference (RPD) between the concentrations (A_1 and A_2):

$$RPD = \frac{|A_1 - A_2|}{\frac{A_1 + A_2}{2}} \times 100$$

8.3.3 Compare the percent recoveries (P_1 and P_2) and the RPD for each analyte in the MS/MSD aliquots with the corresponding QC acceptance criteria for recovery (P) and RPD in Table 4.

(a) If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is suspect and may not be reported or used

for permitting or regulatory compliance. See section 8.1.7 for disposition of failures.

(b) For analytes in Table 2 not listed in Table 4, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13).

8.3.4 After analysis of a minimum of 20 MS/MSD samples for each target analyte and surrogate, and if the laboratory chooses to develop and apply optional in-house QC limits, the laboratory should calculate and apply the optional in-house QC limits for recovery and RPD of future MS/MSD samples (Section 8.3). The optional in-house QC limits for recovery are calculated as the mean observed recovery ± 3 standard deviations, and the upper QC limit for RPD is calculated as the mean RPD plus 3 standard deviations of the RPDs. The in-house QC limits must be updated at least every two years and re-established after any major change in the analytical instrumentation or process. At least 80% of the analytes tested in the MS/MSD must have in-house QC acceptance criteria that are tighter than those in Table 4 and the remaining analytes (those not included in the 80%) must meet the acceptance criteria in Table 4. If an in-house QC limit for the RPD is greater than the limit in Table 4, then the limit in Table 4 must be used. Similarly, if an in-house lower limit for recovery is below the lower limit in Table 4, then the lower limit in Table 4 must be used, and if an in-house upper limit for recovery is above the upper limit in Table 4, then the upper limit in Table 4 must be used. The laboratory must evaluate surrogate recovery data in each sample against its in-house surrogate recovery limits. The laboratory may use 60–140% as interim acceptance criteria for surrogate recoveries until in-house limits are developed. Alternatively, surrogate recovery limits may be developed from laboratory control charts. In-house QC acceptance criteria must be updated at least every two years.

8.4 Laboratory control sample (LCS)—A QC check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) containing each single-component analyte of interest (section 1.4) must be extracted, concentrated, and analyzed with each extraction batch of up to 20 samples (section 3.1) to demonstrate acceptable recovery of the analytes of interest from a clean sample matrix. If multi-peak analytes are required, extract and prepare at least one as an LCS for each batch. Alternatively, the laboratory may set up a program where multi-peak LCS is rotated with a single-peak LCS.

8.4.1 Prepare the LCS by adding QC check sample concentrate (sections 6.8.3 and 8.2.1) to reagent water. Include all analytes of interest (section 1.4) in the LCS. The volume of reagent water must be the same as the nominal volume used for the sample, the DOC (Section 8.2), the blank (section 8.5), and the MS/MSD (section 8.3). Also add a volume of the surrogate solution (section 6.8.6).

8.4.2 Analyze the LCS prior to analysis of samples in the extraction batch (Section 3.1). Determine the concentration (A) of each analyte. Calculate the percent recovery as:

$$P_s = \frac{A}{T} \times 100$$

where T is the true value of the concentration in the LCS.

8.4.3 For each analyte, compare the percent recovery (P) with its corresponding QC acceptance criterion in Table 4. For analytes of interest in Table 2 not listed in Table 4, use the QC acceptance criteria developed for the MS/MSD (section 8.3.3.2), or limits based on laboratory control charts. If the recoveries for all analytes of interest fall within the designated ranges, analysis of blanks and field samples may proceed. If any individual recovery falls outside the range, proceed according to section 8.4.4.

Note: The large number of analytes in Tables 1 and 2 present a substantial probability that one or more will fail the acceptance criteria when all analytes are tested simultaneously. Because a re-test is allowed in event of failure (sections 8.1.7 and 8.4.4), it may be prudent to extract and analyze two LCSs together and evaluate results of the second analysis against the QC acceptance criteria only if an analyte fails the first test.

8.4.4 Repeat the test only for those analytes that failed to meet the acceptance criteria (P). If these analytes now pass, system performance is acceptable and analysis of blanks and samples may proceed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, repeat the test using a fresh LCS (section 8.2.1) or an LCS prepared with a fresh QC check sample concentrate (section 8.2.1), or perform and document system repair. Subsequent to analysis of the LCS prepared with a fresh sample concentrate, or to system repair, repeat the LCS test (Section 8.4). If failure of the LCS indicates a systemic problem with samples in the batch, re-extract and re-analyze the samples in the batch. See Section 8.1.7 for disposition of repeated failures.

8.4.5 After analysis of 20 LCS samples, and if the laboratory chooses to develop and apply optional in-house QC limits, the laboratory should calculate and apply the optional in-house QC limits for recovery of future LCS samples (section 8.4). Limits for recovery in the LCS should be calculated as the mean recovery ± 3 standard deviations. A minimum of 80% of the analytes tested for in the LCS must have QC acceptance criteria tighter than those in Table 4, and the remaining analytes (those not included in the 80%) must meet the acceptance criteria in Table 4. If an in-house lower limit for recovery is lower than the lower limit in Table 4, the lower limit in Table 4 must be used, and if an in-house upper limit for recovery is higher than the upper limit in Table 4, the upper limit in Table 4 must be used. Many of the analytes and surrogates do not contain acceptance criteria. The laboratory should use 60–140% as interim acceptance criteria for recoveries of spiked analytes and surrogates that do not have recovery limits specified in Table 4, and at least 80% of the surrogates must meet the 60–140% interim criteria until in-house LCS and surrogate limits are developed.

Alternatively, acceptance criteria for analytes

that do not have recovery limits in Table 4 may be based on laboratory control charts. In-house QC acceptance criteria must be updated at least every two years.

8.5 Blank—Extract and analyze a blank with each extraction batch (section 3.1) to demonstrate that the reagents and equipment used for preparation and analysis are free from contamination.

8.5.1 Prepare the blank from reagent water and spike it with the surrogates. The volume of reagent water must be the same as the volume used for samples, the DOC (section 8.2), the LCS (section 8.4), and the MS/MSD (section 8.3). Extract, concentrate, and analyze the blank using the same procedures and reagents used for the samples, LCS, and MS/MSD in the batch. Analyze the blank immediately after analysis of the LCS (section 8.4) and prior to analysis of the MS/MSD and samples to demonstrate freedom from contamination.

8.5.2 If any analyte of interest is found in the blank at a concentration greater than the MDL for the analyte, at a concentration greater than one-third the regulatory compliance limit, or at a concentration greater than one-tenth the concentration in a sample in the batch (section 3.1), whichever is greatest, analysis of samples must be halted and samples in the batch must be re-extracted and the extracts reanalyzed. Samples in a batch must be associated with an uncontaminated blank before the results for those samples may be reported or used for permitting or regulatory compliance purposes. If re-testing of blanks results in repeated failures, the laboratory should document the failures and report the problem and failures with the data.

8.6 Surrogate recovery—The laboratory must spike all samples with the surrogate standard spiking solution (section 6.8.6) per section 10.2.2 or 10.4.2, analyze the samples, and calculate the percent recovery of each surrogate. QC acceptance criteria for surrogates must be developed by the laboratory (section 8.4). If any recovery fails its criterion, attempt to find and correct the cause of the failure, and if sufficient volume is available, re-extract another aliquot of the affected sample; otherwise, see section 8.1.7 for disposition of repeated failures.

8.7 As part of the QC program for the laboratory, it is suggested but not required that method accuracy for wastewater samples be assessed and records maintained. After analysis of five or more spiked wastewater samples as in Section 8.3, calculate the average percent recovery (\bar{X}) and the standard deviation of the percent recovery (sp). Express the accuracy assessment as a percent interval from $\bar{X} - 2sp$ to $\bar{X} + 2sp$. For example, if $\bar{X} = 90\%$ and $sp = 10\%$, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each analyte on a regular basis to ensure process control (e.g., after each 5–10 new accuracy measurements). If desired, statements of accuracy for laboratory performance, independent of performance on samples, may be developed using LCSs.

8.8 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend

upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with another dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Collect samples as grab samples in glass bottles, or in refrigerated bottles using automatic sampling equipment. Collect 1-L of ambient waters, effluents, and other aqueous samples. If high concentrations of the analytes of interest are expected (e.g., for untreated effluents or in-process waters), collect a smaller volume (e.g., 250 mL), but not less than 100 mL, in addition to the 1-L sample. Follow conventional sampling practices, except do not pre-rinse the bottle with sample before collection. Automatic sampling equipment must be as free as possible of polyvinyl chloride or other tubing or other potential sources of contamination. If needed, collect additional sample(s) for the MS/MSD (section 8.3).

9.2 Ice or refrigerate the sample at $\leq 6^{\circ}\text{C}$ from the time of collection until extraction, but do not freeze. If aldrin is to be determined and residual chlorine is present, add 80 mg/L of sodium thiosulfate but do not add excess. Any method suitable for field use may be employed to test for residual chlorine (Reference 14). If sodium thiosulfate interferes in the determination of the analytes, an alternative preservative (e.g., ascorbic acid or sodium sulfite) may be used.

9.3 Extract all samples within seven days of collection and completely analyze within 40 days of extraction (Reference 1). If the sample will not be extracted within 72 hours of collection, adjust the sample pH to a range of 5.0–9.0 with sodium hydroxide solution or sulfuric acid. Record the volume of acid or base used.

10. Sample Extraction

10.1 This section contains procedures for separatory funnel liquid-liquid extraction (SFLLE, section 10.2), continuous liquid-liquid extraction (CLLE, section 10.4), and disk-based solid-phase extraction (SPE, section 10.5). SFLLE is faster, but may not be as effective as CLLE for extracting polar analytes. SFLLE is labor intensive and may result in formation of emulsions that are difficult to break. CLLE is less labor intensive, avoids emulsion formation, but requires more time (18–24 hours), more hood space, and may require more solvent. SPE can be faster, unless the particulate load in an aqueous sample is so high that it slows the filtration process. If an alternative extraction scheme to those detailed in this method is used, all QC tests must be performed and all QC acceptance criteria must be met with that extraction scheme as an integral part of this method.

10.2 Separatory funnel liquid-liquid extraction (SFLLE).

10.2.1 The SFLLE procedure below assumes a sample volume of 1 L. When a different sample volume is extracted, adjust the volume of methylene chloride accordingly.

10.2.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into the separatory funnel. Pipet the surrogate standard spiking solution (section 6.8.6) into the separatory funnel. If the sample will be used for the LCS or MS or MSD, pipet the appropriate QC check sample concentrate (section 8.3 or 8.4) into the separatory funnel. Mix well. If the sample arrives in a larger sample bottle, 1 L may be measured in a graduated cylinder, then added to the separatory funnel.

Note: Instances in which the sample is collected in an oversized bottle should be reported by the laboratory to the data user. Of particular concern is that fact that this practice precludes rinsing the empty bottle with solvent as described below, which could leave hydrophobic pesticides on the wall of the bottle, and underestimate the actual sample concentrations.

10.2.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If an emulsion forms and the emulsion interface between the layers is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, use of phase-separation paper, centrifugation, salting, freezing, or other physical methods. Collect the methylene chloride extract in a flask. If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in section 10.4.

10.2.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the flask. Perform a third extraction in the same manner. Proceed to macro-concentration (section 10.3.1).

10.2.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to an appropriately sized graduated cylinder. Record the sample volume to the nearest 5 mL. Sample volumes may also be determined by weighing the container before and after extraction or filling to the mark with water.

10.3 Concentration.

10.3.1 Macro concentration.

10.3.1.1 Assemble a Kuderna-Danish (K–D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K–D concentrator so long as the requirements of section 8.2 are met.

10.3.1.2 Pour the extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K–D concentrator. Rinse the flask and column with 20–30 mL of methylene chloride to complete the quantitative transfer.

10.3.1.3 If no cleanup is to be performed on the sample, add 500 μL (0.5 mL) of iso-octane to the extract to act as a keeper during concentration.

10.3.1.4 Add one or two clean boiling chips and attach a three-ball Snyder column to the K–D evaporative flask. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath ($60\text{--}65^{\circ}\text{C}$) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of evaporation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL or other determined amount, remove the K–D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

10.3.1.5 If the extract is to be cleaned up by sulfur removal or acid back extraction, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Adjust the final volume to 10 mL in methylene chloride and proceed to sulfur removal (section 11.5) or acid back extraction (section 11.6). If the extract is to be cleaned up using one of the other cleanup procedures or is to be injected into the GC, proceed to Kuderna-Danish micro-concentration (section 10.3.2) or nitrogen evaporation and solvent exchange (section 10.3.3).

10.3.2 Kuderna-Danish micro concentration—Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro-Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath ($60\text{--}65^{\circ}\text{C}$) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5–10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches approximately 1 mL or other required amount, remove the K–D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of methylene chloride, and proceed to section 10.3.3 for nitrogen evaporation and solvent exchange.

10.3.3 Nitrogen evaporation and solvent exchange—Extracts to be subjected to solid-phase cleanup (SPE) are exchanged into 1.0 mL of the SPE elution solvent (section 6.7.2.2). Extracts to be subjected to Florisil®

or alumina cleanups are exchanged into hexane. Extracts that have been cleaned up and are ready for analysis are exchanged into isooctane or hexane, to match the solvent used for the calibration standards.

10.3.3.1 Transfer the vial containing the sample extract to the nitrogen evaporation (blowdown) device (section 5.2.5.2). Lower the vial into a 50–55 °C water bath and begin concentrating. During the solvent evaporation process, do not allow the extract to become dry. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed. A large vortex in the solvent may cause analyte loss.

10.3.3.2 Solvent exchange.

10.3.3.2.1 When the volume of the liquid is approximately 500 µL, add 2 to 3 mL of the desired solvent (SPE elution solvent for SPE cleanup, hexane for Florisil or alumina, or isooctane for final injection into the GC) and continue concentrating to approximately 500 µL. Repeat the addition of solvent and concentrate once more.

10.3.3.3.2 Adjust the volume of an extract to be cleaned up by SPE, Florisil®, or alumina to 1.0 mL. Proceed to extract cleanup (section 11).

10.3.3.3 Extracts that have been cleaned up and are ready for analysis—Adjust the final extract volume to be consistent with the volume extracted and the sensitivity desired. The goal is for a full-volume sample (e.g., 1-L) to have a final extract volume of 10 mL, but other volumes may be used.

10.3.4 Transfer the concentrated extract to a vial with fluoropolymer-lined cap. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for GC analysis. If GC analysis will not be performed on the same day, store the vial in the dark at ≤6 °C. Analyze the extract by GC per the procedure in section 12.

10.4 Continuous liquid/liquid extraction (CLLE).

10.4.1 Use CLLE when experience with a sample from a given source indicates an emulsion problem, or when an emulsion is encountered using SFLE. CLLE may be used for all samples, if desired.

10.4.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Transfer the sample to the continuous extractor and, using a pipet, add surrogate standard spiking solution. If the sample will be used for the LCS, MS, or MSD, pipet the appropriate check sample concentrate (section 8.2.1 or 8.3.2) into the separatory funnel. Mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor.

10.4.3 Repeat the sample bottle rinse with two additional 50–100 mL portions of methylene chloride and add the rinses to the extractor.

10.4.4 Add a suitable volume of methylene chloride to the distilling flask (generally 200–500 mL) and sufficient reagent water to ensure proper operation of the extractor, and extract the sample for 18–24 hours. A shorter or longer extraction time may be used if all QC acceptance criteria are met. Test and, if necessary, adjust the pH of the water to a range of 5.0–9.0 during the

second or third hour of the extraction. After extraction, allow the apparatus to cool, then detach the distilling flask. Dry, concentrate, solvent exchange, and transfer the extract to a vial with fluoropolymer-lined cap, per Section 10.3.

10.4.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to an appropriately sized graduated cylinder. Record the sample volume to the nearest 5 mL. Sample volumes may also be determined by weighing the container before and after extraction or filling to the mark with water.

10.5 Solid-phase extraction of aqueous samples. The steps in this section address the extraction of aqueous field samples using disk-based solid-phase extraction (SPE) media, based on an ATP approved by EPA in 1995 (Reference 20). This application of SPE is distinct from that used in this method for the cleanup of sample extracts in section 11.2. Analysts must be careful not to confuse the equipment, supplies, or the procedural steps from these two different uses of SPE.

Note: Changes to the extraction conditions described below may be made by the laboratory under the allowance for method flexibility described in section 8.1, provided that the performance requirements in section 8.2 are met. However, changes in SPE materials, formats, and solvents must meet the requirements in section 8.1.2 and its subsections.

10.5.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. If the sample contains particulates, let stand to settle out the particulates before extraction.

10.5.2 Extract the sample as follows:

10.5.2.1 Place a 90-mm standard filter apparatus on a vacuum filtration flask or manifold and attach to a vacuum source. The vacuum gauge must read at least 25 in. of mercury when all valves are closed. Position a 90-mm C18 extraction disk onto the filter screen. Wet the entire disk with methanol. To aid in filtering samples with particulates, a 1-µm glass fiber filter or Empore® Filter Aid 400 can be placed on the top of the disk and wetted with methanol. Install the reservoir and clamp. Resume vacuum to dry the disk. Interrupt the vacuum. Wash the disk and reservoir with 20 mL of methylene chloride. Resume the vacuum briefly to pull methylene chloride through the disk. Interrupt the vacuum and allow the disk to soak for about a minute. Resume vacuum and completely dry the disk.

10.5.2.2 Condition the disk with 20 mL of methanol. Apply vacuum until nearly all the solvent has passed through the disk, interrupting it while solvent remains on the disk. Allow the disk to soak for about a minute. Resume vacuum to pull most of the methanol through, but interrupting it to leave a layer of methanol on the surface of the disk. Do not allow disk to dry. For uniform flow and good recovery, it is critical the disk not be allowed to dry from now until the end of the extraction. Discard waste solvent. Rinse the disk with 20 mL of deionized water. Resume vacuum to pull most of the water through, but interrupt it to leave a layer of water on the surface of the disk. Do not allow the disk to dry. If disk does dry, recondition with methanol as above.

10.5.2.3 Add the water sample to the reservoir and immediately apply the vacuum. If particulates have settled in the sample, gently decant the clear layer into the apparatus until most of the sample has been processed. Then pour the remainder including the particulates into the reservoir. Empty the sample bottle completely. When the filtration is complete, dry the disk for three minutes. Turn off the vacuum.

10.5.3 Discard sample filtrate. Insert tube to collect the eluant. The tube should fit around the drip tip of the base. Reassemble the apparatus. Add 5.0 mL of acetone to the center of the disk, allowing it to spread evenly over the disk. Turn the vacuum on and quickly off when the filter surface nears dryness but still remains wet. Allow to soak for 15 seconds. Add 20 mL of methylene chloride to the sample bottle, seal and shake to rinse the inside of the bottle. Transfer the methylene chloride from the bottle to the filter. Resume the vacuum slowly so as to avoid splashing.

Interrupt the vacuum when the filter surface nears dryness but still remains wet. Allow disk to soak in solvent for 20 seconds. Rinse the reservoir glass and disk with 10 mL of methylene chloride. Resume vacuum slowly. Interrupt vacuum when disk is covered with solvent. Allow to soak for 20 seconds. Resume vacuum to dry the disk. Remove the sample tube.

10.5.4 Dry, concentrate, solvent exchange, and transfer the extract to a vial with fluoropolymer-lined cap, per section 10.3.

10.5.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to an appropriately sized graduated cylinder. Record the sample volume to the nearest 5 mL. Sample volumes may also be determined by weighing the container before and after extraction or filling to the mark with water.

11. Extract Cleanup

11.1 Cleanup may not be necessary for relatively clean samples (e.g., treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the laboratory may use any or all of the procedures below or any other appropriate procedure (e.g., gel permeation chromatography). However, the laboratory must first repeat the tests in sections 8.2, 8.3, and 8.4 to demonstrate that the requirements of those sections can be met using the cleanup procedure(s) as an integral part of this method. This is particularly important when the target analytes for the analysis include any of the single component pesticides in Table 2, because some cleanups have not been optimized for all of those analytes.

11.1.1 The solid-phase cartridge (section 11.2) removes polar organic compounds such as phenols.

11.1.2 The Florisil® column (section 11.3) allows for selected fractionation of the organochlorine analytes and will also eliminate polar interferences.

11.1.3 Alumina column cleanup (section 11.4) also removes polar materials.

11.1.4 Elemental sulfur, which interferes with the electron capture gas chromatography of some of the pesticides,

may be removed using activated copper, or TBA sulfite. Sulfur removal (section 11.5) is required when sulfur is known or suspected to be present. Some chlorinated pesticides which also contain sulfur may be removed by this cleanup.

11.1.5 Acid back extraction (section 11.6) may be useful for cleanup of PCBs and other compounds not adversely affected by sulfuric acid.

11.2 Solid-phase extraction (SPE) as a cleanup. In order to use the C18 SPE cartridge in section 5.5.3.5 as a cleanup procedure, the sample extract must be exchanged from methylene chloride to methylene chloride:acetonitrile:hexane (50:3:47). Follow the solvent exchange steps in section 10.3.3.2 prior to attempting solid-phase cleanup.

Note: This application of SPE is distinct from that used in this method for the extraction of aqueous samples in section 10.5. Analysts must be careful not to confuse the equipment, supplies, or procedural steps from these two different uses of SPE.

11.2.1 Setup.

11.2.1.1 Attach the VacElute Manifold (section 5.5.3.2) to a water aspirator or vacuum pump with the trap and gauge installed between the manifold and vacuum source.

11.2.1.2 Place the SPE cartridges in the manifold, turn on the vacuum source, and adjust the vacuum to 5 to 10 psi.

11.2.2 Cartridge washing—Pre-elute each cartridge prior to use sequentially with 10-mL portions each of hexane, methanol, and water using vacuum for 30 seconds after each eluting solvent. Follow this pre-elution with 1 mL methylene chloride and three 10-mL portions of the elution solvent (section 6.7.2.2) using vacuum for 5 minutes after each eluting solvent. Tap the cartridge lightly while under vacuum to dry between solvent rinses. The three portions of elution solvent may be collected and used as a cartridge blank, if desired. Finally, elute the cartridge with 10 mL each of methanol and water, using the vacuum for 30 seconds after each eluant.

11.2.3 Extract cleanup.

11.2.3.1 After cartridge washing (section 11.2.2), release the vacuum and place the rack containing the 50-mL volumetric flasks (section 5.5.3.4) in the vacuum manifold. Re-establish the vacuum at 5 to 10 psi.

11.2.3.2 Using a pipette or a 1-mL syringe, transfer 1.0 mL of extract to the SPE cartridge. Apply vacuum for five minutes to dry the cartridge. Tap gently to aid in drying.

11.2.3.3 Elute each cartridge into its volumetric flask sequentially with three 10-mL portions of the methylene chloride:acetonitrile:hexane (50:3:47) elution solvent (section 6.7.2.2), using vacuum for five minutes after each portion. Collect the eluants in the 50-mL volumetric flasks.

11.2.3.4 Release the vacuum and remove the 50-mL volumetric flasks.

11.2.3.5 Concentrate the eluted extracts per Section 10.3.

11.3 Florisil®. In order to use Florisil cleanup, the sample extract must be exchanged from methylene chloride to hexane. Follow the solvent exchange steps in section 10.3.3.2 prior to attempting Florisil® cleanup.

Note: Alternative formats for this cleanup may be used by the laboratory, including cartridges containing Florisil®. If an alternative format is used, consult the manufacturer's instructions and develop a formal documented procedure to replace the steps in section 11.3 of this method and demonstrate that the alternative meets the relevant quality control requirements of this method.

11.3.1 If the chromatographic column does not contain a frit at the bottom, place a small plug of pre-cleaned glass wool in the column (section 5.2.4) to retain the Florisil®. Place the mass of Florisil® (nominally 20 g) predetermined by calibration (section 7.8 and Table 6) in a chromatographic column. Tap the column to settle the Florisil® and add 1 to 2 cm of granular anhydrous sodium sulfate to the top.

11.3.2 Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil®. Just prior to exposure of the sodium sulfate layer to the air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluant.

11.3.3 Transfer the concentrated extract (section 10.3.3) onto the column. Complete the transfer with two 1-mL hexane rinses, drawing the extract and rinses down to the level of the sodium sulfate.

11.3.4 Place a clean 500-mL K-D flask and concentrator tube under the column. Elute Fraction 1 with 200 mL of 6% (v/v) ethyl ether in hexane at a rate of approximately 5 mL/min. Remove the K-D flask and set it aside for later concentration. Elute Fraction 2 with 200 mL of 15% (v/v) ethyl ether in hexane into a second K-D flask. Elute Fraction 3 with 200 mL of 50% (v/v) ethyl ether in hexane into a third K-D flask. The elution patterns for the pesticides and PCBs are shown in Table 6.

11.3.5 Concentrate the fractions as in Section 10.3, except use hexane to prewet the column and set the water bath at about 85 °C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the volume of Fraction 1 to approximately 10 mL for sulfur removal (Section 11.5), if required; otherwise, adjust the volume of the fractions to 10 mL, 1.0 mL, or other volume needed for the sensitivity desired. Analyze the concentrated extract by gas chromatography (Section 12).

11.4 Alumina. The sample extract must be exchanged from methylene chloride to hexane. Follow the solvent exchange steps in section 10.3.3.2 prior to attempting alumina cleanup.

11.4.1 If the chromatographic column does not contain a frit at the bottom, place a small plug of pre-cleaned glass wool in the chromatographic column (section 5.2.4) to retain the alumina. Add 10 g of alumina (section 6.7.3) on top of the plug. Tap the column to settle the alumina. Place 1–2 g of anhydrous sodium sulfate on top of the alumina.

11.4.2 Close the stopcock and fill the column to just above the sodium sulfate with hexane. Add 25 mL of hexane. Open the stopcock and adjust the flow rate of hexane to approximately 2 mL/min. Do not allow the column to go dry throughout the elutions.

11.4.3 When the level of the hexane is at the top of the column, quantitatively transfer the extract to the column. When the level of the extract is at the top of the column, slowly add 25 mL of hexane and elute the column to the level of the sodium sulfate. Discard the hexane.

11.4.4 Place a K-D flask (section 5.2.5.1.2) under the column and elute the pesticides with approximately 150 mL of hexane:ethyl ether (80:20 v/v). It may be necessary to adjust the volume of elution solvent for slightly different alumina activities.

11.4.5 Concentrate the extract per section 10.3.

11.5 Sulfur removal—Elemental sulfur will usually elute in Fraction 1 of the Florisil® column cleanup. If Florisil® cleanup is not used, or to remove sulfur from any of the Florisil® fractions, use one of the sulfur removal procedures below. These procedures may be applied to extracts in hexane, ethyl ether, or methylene chloride.

Note: Separate procedures using copper or TBA sulfite are provided in this section for sulfur removal. They may be used separately or in combination, if desired.

11.5.1 Removal with copper (Reference 15).

Note: Some of the analytes in Table 2 are not amenable to sulfur removal with copper (e.g., atrazine and diazinon). Therefore, before using copper to remove sulfur from an extract that will be analyzed for any of the non-PCB analytes in Table 2, the laboratory must demonstrate that the analytes can be extracted from an aqueous sample matrix that contains sulfur and recovered from an extract treated with copper. Acceptable performance can be demonstrated through the preparation and analysis of a matrix spike sample that meets the QC requirements for recovery.

11.5.1.1 Quantitatively transfer the extract to a 40- to 50-mL flask or bottle. If there is evidence of water in the K-D or round-bottom flask after the transfer, rinse the flask with small portions of hexane:acetone (40:60) and add to the flask or bottle. Mark and set aside the concentration flask for future use.

11.5.1.2 Add 10–20 g of granular anhydrous sodium sulfate to the flask. Swirl to dry the extract.

11.5.1.3 Add activated copper (section 6.7.4.1.4) and allow to stand for 30–60 minutes, swirling occasionally. If the copper does not remain bright, add more and swirl occasionally for another 30–60 minutes.

11.5.1.4 After drying and sulfur removal, quantitatively transfer the extract to a nitrogen-evaporation vial or tube and proceed to section 10.3.3 for nitrogen evaporation and solvent exchange, taking care to leave the sodium sulfate and copper foil in the flask.

11.5.2 Removal with TBA sulfite.

11.5.2.1 Using small volumes of hexane, quantitatively transfer the extract to a 40- to 50-mL centrifuge tube with fluoropolymer-lined screw cap.

11.5.2.2 Add 1–2 mL of TBA sulfite reagent (section 6.7.4.2.4), 2–3 mL of 2-propanol, and approximately 0.7 g of sodium sulfite (section 6.7.4.2.2) crystals to

the tube. Cap and shake for 1–2 minutes. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 0.5-g portions until a solid residue remains after repeated shaking.

11.5.2.3 Add 5–10 mL of reagent water and shake for 1–2 minutes. Centrifuge to settle the solids.

11.5.2.4 Quantitatively transfer the hexane (top) layer through a small funnel containing a few grams of granular anhydrous sodium sulfate to a nitrogen-evaporation vial or tube and proceed to section 10.3.3 for micro-concentration and solvent exchange.

11.6 Acid back extraction (section 6.1.2).

11.6.1 Quantitatively transfer the extract (section 10.3.1.5) to a 250-mL separatory funnel.

11.6.2 Partition the extract against 50 mL of sulfuric acid solution (section 6.1.2). Discard the aqueous layer. Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.

11.6.3 Partition the extract against 50 mL of sodium chloride solution (section 6.7.5). Discard the aqueous layer.

11.6.4 Proceed to section 10.3.3 for micro-concentration and solvent exchange.

12. Gas Chromatography

12.1 Establish the same operating conditions used in section 7.1 for instrument calibration.

12.2 If the internal standard calibration procedure is used, add the internal standard solution (section 6.9.3) to the extract as close as possible to the time of injection to minimize the possibility of loss by

evaporation, adsorption, or reaction. For example, add 1 µL of 10 µg/mL internal standard solution into the extract, assuming no dilutions. Mix thoroughly.

12.3 Simultaneously inject an appropriate volume of the sample extract or standard solution onto both columns, using split, splitless, solvent purge, large-volume, or on-column injection. Alternatively, if using a single-column GC configuration, inject an appropriate volume of the sample extract or standard solution onto each GC column independently. If the sample is injected manually, the solvent-flush technique should be used. The injection volume depends upon the technique used and the sensitivity needed to meet MDLs or reporting limits for regulatory compliance. Injection volumes must be the same for all extracts. Record the volume injected to the nearest 0.05 µL.

12.4 Set the data system or GC control to start the temperature program upon sample injection, and begin data collection after the solvent peak elutes. Set the data system to stop data collection after the last analyte is expected to elute and to return the column to the initial temperature.

12.5 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When standards and extracts are not being used for analyses, store them refrigerated at <6 °C, protected from light, in screw-cap vials equipped with unpierced fluoropolymer-lined septa.

13. System and Laboratory Performance

13.1 At the beginning of each shift during which standards or extracts are analyzed, GC system performance and calibration must be verified for all analytes and surrogates on both column/detector systems. Adjustment and/or recalibration (per section 7) are performed until all performance criteria are met. Only after all performance criteria are

met may samples, blanks and other QC samples, and standards be analyzed.

13.2 Inject an aliquot of the calibration verification standard (section 6.8.4) on both columns. Inject an aliquot of each of the multi-component standards.

13.3 Retention times—The absolute retention times of the peak maxima shall be within ±2 seconds of the retention times in the calibration verification (section 7.8).

13.4 GC resolution—Resolution is acceptable if the valley height between two peaks (as measured from the baseline) is less than 40% of the shorter of the two peaks.

13.4.1 DB-608 column—DDT and endrin aldehyde

13.4.2 DB-1701 column—*alpha* and *gamma* chlordane

Note: If using other GC columns or stationary phases, these resolution criteria apply to these four target analytes and any other closely eluting analytes on those other GC columns.

13.5 Decomposition of DDT and endrin—If DDT, endrin, or their breakdown products are to be determined, this test must be performed prior to calibration verification (section 13.6). DDT decomposes to DDE and DDD. Endrin decomposes to endrin aldehyde and endrin ketone.

13.5.1 Inject 1 µL of the DDT and endrin decomposition solution (section 6.8.7). As noted in section 6.8.7, other injection volumes may be used as long as the concentrations of DDT and endrin in the solution are adjusted to introduce the masses of the two analytes into the instrument that are listed in section 6.8.7.

13.5.2 Measure the areas of the peaks for DDT, DDE, DDD, endrin, endrin aldehyde, and endrin ketone in the chromatogram and calculate the percent breakdown as shown in the equations below:

$$\% \text{ breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD + DDE)}}{\text{sum of all peak areas (DDT + DDE + DDD)}} \times 100$$

% breakdown of Endrin

$$= \frac{\text{sum of degradation peak areas (Endrin aldehyde + Endrin ketone)}}{\text{sum of all peak areas (Endrin + Endrin aldehyde + Endrin ketone)}} \times 100$$

13.5.3 Both the % breakdown of DDT and of endrin must be less than 20%, otherwise the system is not performing acceptably for DDT and endrin. In this case, repair the GC column system that failed and repeat the performance tests (sections 13.2 to 13.6) until the specification is met.

Note: DDT and endrin decomposition are usually caused by accumulations of particulates in the injector and in the front end of the column. Cleaning and silanizing the injection port liner, and breaking off a short section of the front end of the column will usually eliminate the decomposition problem. Either of these corrective actions may affect retention times, GC resolution, and calibration linearity.

13.6 Calibration verification.

13.6.1 Compute the percent recovery of each analyte and of the coeluting analytes, based on the initial calibration data (section 7.5 or 7.6).

13.6.2 For each analyte or for coeluting analytes, compare the concentration with the limits for calibration verification in Table 4. For coeluting analytes, use the coeluting analyte with the least restrictive specification (the widest range). For analytes in Table 2 not listed in Table 4, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 13 and 14). If the recoveries for all analytes meet the acceptance criteria, system performance is

acceptable and analysis of blanks and samples may continue. If, however, any recovery falls outside the calibration verification range, system performance is unacceptable for that analyte. If this occurs, repair the system and repeat the test (section 13.6), or prepare a fresh calibration standard and repeat the test, or recalibrate (section 7). See Section 8.1.7 for information on repeated test failures.

13.7 Laboratory control sample.

13.7.1 Analyze the extract of the LCS (section 6.8.3) extracted with each sample batch (Section 8.4). See Section 8.4 for criteria acceptance of the LCS.

13.7.2 It is suggested, but not required, that the laboratory update statements of data

quality. Add results that pass the specifications in section 13.7.3 to initial (section 8.7) and previous ongoing data. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of percent recovery, sr. Express the accuracy as a recovery interval from $R - 2sr$ to $R + 2sr$. For example, if $R = 95\%$ and $sr = 5\%$, the accuracy is 85 to 105%.

13.8 Internal standard response—If internal standard calibration is used, verify that detector sensitivity has not changed by comparing the response (area or height) of each internal standard in the sample, blank, LCS, MS, and MSD to the response in calibration verification (section 6.8.3). The peak area or height of the internal standard should be within 50% to 200% ($\frac{1}{2}$ to $2x$) of its respective peak area or height in the verification standard. If the area or height is not within this range, compute the concentration of the analytes using the external standard method (section 7.5). If the analytes are affected, re-prepare and reanalyze the sample, blank, LCS, MS, or MSD, and repeat the pertinent test.

14. Qualitative Identification

14.1 Identification is accomplished by comparison of data from analysis of a sample, blank, or other QC sample with data from calibration verification (section 7.7.1 or 13.5), and with data stored in the retention-time and calibration libraries (section 7.7). The retention time window is determined as described in section 14.2. Identification is confirmed when retention time agrees on both GC columns, as described below. Alternatively, GC/MS identification may be used to provide another means of identification.

14.2 Establishing retention time windows.

14.2.1 Using the data from the multi-point initial calibration (section 7.4), determine the retention time in decimal minutes (not minutes:seconds) of each peak representing a single-component target analyte on each column/detector system. For the multi-component analytes, use the retention times of the five largest peaks in the chromatograms on each column/detector system.

14.2.2 Calculate the standard deviation of the retention times for each single-component analyte on each column/detector system and for the three to five exclusive (unique large) peaks for each multi-component analyte.

14.2.3 Define the width of the retention time window as three times that standard deviation. Establish the center of the retention time window for each analyte by using the absolute retention time for each analyte from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration. If the calculated RT window is less than 0.02 minutes, then use 0.02 minutes as the window.

Note: Procedures for establishing retention time windows from other sources may be employed provided that they are clearly documented and provide acceptable performance. Such performance may be evaluated using the results for the spiked QC samples described in this method, such as laboratory control samples and matrix spike samples.

14.2.4 The retention time windows must be recentered when a new GC column is installed or if a GC column has been shortened during maintenance to a degree that the retention times of analytes in the calibration verification standard have shifted close to the lower limits of the established retention time windows.

14.2.5 RT windows should be checked periodically by examining the peaks in spiked samples such as the LCS or MS/MSD to confirm that peaks for known analytes are properly identified.

14.2.6 If the retention time of an analyte in the calibration (Section 7.4) varies by more than 5 seconds across the calibration range as a function of the concentration of the standard, using the standard deviation of the retention times (section 14.2.3) to set the width of the retention time window may not adequately serve to identify the analyte in question under routine conditions. In such cases, data from additional analyses of standards may be required to adequately model the chromatographic behavior of the analyte.

14.3 Identifying the analyte in a sample.

14.3.1 In order to identify a single-component analyte from analysis of a sample, blank, or other QC sample, the peak representing the analyte must fall within its respective retention time windows on both column/detector systems (as defined in section 14.2). That identification is further supported by the comparison of the numerical results on both columns, as described in section 15.7.

14.3.2 In order to identify a multi-component analyte, pattern matching (fingerprinting) may be used, or the three to five exclusive (unique and largest) peaks for that analyte must fall within their respective retention time windows on both column/detector systems (as defined in section 14.2). That identification is further supported by the comparison of the numerical results on both columns, as described in section 15.7. Alternatively, GC/MS identification may be used. Differentiation among some of the Aroclors may require evaluation of more than five peaks to ensure correct identification.

14.4 GC/MS confirmation. When the concentration of an analyte is sufficient and the presence or identity is suspect, its presence should be confirmed by GC/MS. In order to match the sensitivity of the GC/ECD, confirmation would need to be by GC/MS-SIM, or the estimated concentration would need to be 100 times higher than the GC/ECD calibration range. The extract may be concentrated by an additional amount to allow a further attempt at GC/MS confirmation.

14.5 Additional information that may aid the laboratory in the identification of an analyte. The occurrence of peaks eluting near the retention time of an analyte of interest

increases the probability of a false positive for the analyte. If the concentration is insufficient for confirmation by GC/MS, the laboratory may use the cleanup procedures in this method (section 11) on a new sample aliquot to attempt to remove the interferent. After attempts at cleanup are exhausted, the following steps may be helpful to assure that the substance that appears in the RT windows on both columns is the analyte of interest.

14.5.1 Determine the consistency of the RT data for the analyte on each column. For example, if the RT is very stable (*i.e.*, varies by no more than a few seconds) for the calibration, calibration verification, blank, LCS, and MS/MSD, the RT for the analyte of interest in the sample should be within this variation regardless of the window established in Section 14.2. If the analyte is not within this variation on both columns, it is likely not present.

14.5.2 The possibility exists that the RT for the analyte in a sample could shift if extraneous materials are present. This possibility may be able to be confirmed or refuted by the behavior of the surrogates in the sample. If multiple surrogates are used that span the length of the chromatographic run, the RTs for the surrogates on both columns are consistent with their RTs in calibration, calibration verification, blank, LCS, and MS/MSD, it is unlikely that the RT for the analyte of interest has shifted.

14.5.3 If the RT for the analyte is shifted slightly later on one column and earlier on the other, and the surrogates have not shifted, it is highly unlikely that the analyte is present, because shifts nearly always occur in the same direction on both columns.

15. Quantitative Determination

15.1 External standard quantitation—Calculate the concentration of the analyte in the extract using the calibration curve or average calibration factor determined in calibration (section 7.5.2) and the following equation:

$$C_{\text{ex}} = \frac{A_s}{CF}$$

where:

C_{ex} = Concentration of the analyte in the extract (ng/mL)

A_s = Peak height or area for the analyte in the standard or sample

CF = Calibration factor, as defined in Section 7.5.1

15.2 Internal standard quantitation—Calculate the concentration of the analyte in the extract using the calibration curve or average response factor determined in calibration (section 7.6.2) and the following equation:

$$C_{\text{ex}} = \frac{A_s \times C_{\text{is}}}{A_{\text{is}} \times RF}$$

where:

C_{ex} = Concentration of the analyte in the extract (ng/mL)

A_s = Peak height or area for the analyte in the standard or sample

C_{is} = Concentration of the internal standard (ng/mL)

A_{is} = Area of the internal standard
 RF = Response factor, as defined in section 7.6.1

15.3 Calculate the concentration of the analyte in the sample using the concentration in the extract, the extract volume, the sample volume, and the dilution factor, per the following equation:

$$C_s = \frac{C_{ex} \times V_{ex} \times DF}{V_s \times 1000}$$

where:

C_s = Concentration of the analyte in the sample ($\mu\text{g/L}$)
 V_{ex} = Final extract volume (mL)
 C_{ex} = Concentration in the extract (ng/mL)
 V_s = Volume of sample (L)
 DF = Dilution factor

and the factor of 1,000 in the denominator converts the final units from ng/L to $\mu\text{g/L}$

15.4 If the concentration of any target analyte exceeds the calibration range, either extract and analyze a smaller sample volume, or dilute and analyze the diluted extract.

15.5 Quantitation of multi-component analytes.

15.5.1 PCBs as Aroclors. Quantify an Aroclor by comparing the sample chromatogram to that of the most similar Aroclor standard as indicated in section 14.3.2. Compare the responses of 3 to 5 major peaks in the calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen in section 7.5.1. Determine the concentration of each of the characteristic peaks, using the average calibration factor calculated for that peak in section 7.5.2, and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

15.5.2 Other multi-component analytes. Quantify any other multi-component analytes (technical chlordane or toxaphene) using the same peaks used to develop the average calibration factors in section 7.5.2. Determine the concentration of each of the characteristic peaks, and then the concentrations represented by those characteristic peaks are averaged to determine the concentration of the analyte. Alternatively, for toxaphene, the analyst may determine the calibration factor in section 7.5.2 by summing the areas of all of the peaks for the analyte and using the

summed of the peak areas in the sample chromatogram to determine the concentration. However, the approach used for toxaphene must be the same for the calibration and the sample analyses.

15.6 Reporting of results. As noted in section 1.6.1, EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described here are focused on such monitoring needs and may not be relevant to other uses of the method.

15.6.1 Report results for wastewater samples in $\mu\text{g/L}$ without correction for recovery. (Other units may be used if required by a permit.) Report all QC data with the sample results.

15.6.2 Reporting level. Unless specified otherwise by a regulatory authority or in a discharge permit, results for analytes that meet the identification criteria are reported down to the concentration of the ML established by the laboratory through calibration of the instrument (see section 7.5 or 7.6 and the glossary for the derivation of the ML). EPA considers the terms "reporting limit," "quantitation limit," and "minimum level" to be synonymous.

15.6.2.1 Report the lower result from the two columns (see section 15.7 below) for each analyte in each sample or QC standard at or above the ML to 3 significant figures. Report a result for each analyte in each sample or QC standard below the ML as "<ML," where "ML" is the concentration of the analyte at the ML (e.g., if the ML is 10 $\mu\text{g/L}$, then report the result as <10 $\mu\text{g/L}$), or as required by the regulatory authority or permit. Report a result for each analyte in a blank at or above the MDL to 2 significant figures. Report a result for each analyte found in a blank below the MDL as "<MDL," where MDL is the concentration of the analyte at the MDL, or as required by the regulatory/control authority or permit.

15.6.2.2 In addition to reporting results for samples and blank(s) separately, the concentration of each analyte in a blank or field blank associated with that sample may be subtracted from the result for that sample, but only if requested or required by a regulatory authority or in a permit. In this case, both the sample result and the blank results must be reported together.

15.6.2.3 Report the result for an analyte in a sample or extract that has been diluted

at the least dilute level at which the peak area is within the calibration range (i.e., above the ML for the analyte) and the MS/MSD recovery and RPD are within their respective QC acceptance criteria (Table 4). This may require reporting results for some analytes from different analyses. Results for each analyte in MS/MSD samples should be reported from the same GC column as used to report the results for that analyte in the unspiked sample. If the MS/MSD recoveries and RPDs calculated in this manner do not meet the acceptance criteria in Table 4, the analyst may use the results from the other GC column to determine if the MS/MSD results meet the acceptance criteria. If such a situation occurs, the results for the sample should be recalculated using the same GC column data as used for the MS/MSD samples, and reported with appropriate annotations that alert the data user of the issue.

15.6.2.4 Results from tests performed with an analytical system that is not in control (i.e., that does not meet acceptance criteria for all of QC tests in this method) must not be reported or otherwise used for permitting or regulatory compliance purposes, but do not relieve a discharger or permittee of reporting timely results. See section 8.1.7 for dispositions of failures. If the holding time would be exceeded for a re-analysis of the sample, the regulatory/control authority should be consulted for disposition.

15.6.3 Analyze the sample by GC/MS or on a third column when analytes have co-eluted or interfere with determination on both columns.

Note: Dichlone and kepone do not elute from the DB-1701 column and must be confirmed on a DB-5 column, or by GC/MS.

15.7 Quantitative information that may aid in the confirmation of the presence of an analyte.

15.7.1 As noted in Section 14.3, the relative agreement between the numerical results from the two GC columns may be used to support the identification of the target analyte by providing evidence that co-eluting interferences are not present at the retention time of the target analyte. Calculate the percent difference (%D) between the results for the analyte from both columns, as follows:

$$\%D = \frac{\text{Higher result} - \text{Lower result}}{\text{Higher result}} \times 100$$

In general, if the %D of the two results is less than 50% (e.g., a factor of 2), then the pesticide is present. This %D is generous and allows for the pesticide that has the largest measurement error.

Note: Laboratories may employ metrics less than 50% for this comparison, including those specified in other analytical methods for these pesticides (e.g., CLP or SW-846).

15.7.2 If the amounts do not agree, and the RT data indicate the presence of the

analyte (per Section 14), it is likely that a positive interference is present on the column that yielded the higher result. That interferent may be represented by a separate peak on the other column that does not coincide with the retention time of any of the target analytes. If the interfering peak is evident on the other column, report the result from that column and advise the data user that the interference resulted in a %D value greater than 50%. If an interferent is not

identifiable on the second column, then the results must be reported as "not detected" at the lower concentration. In this event, the pesticide is not confirmed and the reporting limit is elevated. See section 8.1.7 for disposition of problem results.

Note: The resulting elevation of the reporting limit may not meet the requirements for compliance monitoring and the use of additional cleanup procedures may be required.

16. Analysis of Complex Samples

16.1 Some samples may contain high levels (greater than 1 µg/L) of the analytes of interest, interfering analytes, and/or polymeric materials. Some samples may not concentrate to 1.0 mL (section 10.3.3.3.2); others may overload the GC column and/or detector.

16.2 When an interference is known or suspected to be present, the laboratory should attempt to clean up the sample extract using the SPE cartridge (section 11.2), by Florisil® (Section 11.3), Alumina (Section 11.4), sulfur removal (section 11.5), or another clean up procedure appropriate to the analytes of interest. If these techniques do not remove the interference, the extract is diluted by a known factor and reanalyzed (section 12). Dilution until the extract is lightly colored is preferable. Typical dilution factors are 2, 5, and 10.

16.3 Recovery of surrogate(s)—In most samples, surrogate recoveries will be similar to those from reagent water. If surrogate recovery is outside the limits developed in Section 8.6, re-extract and reanalyze the sample if there is sufficient sample and if it is within the 7-day extraction holding time. If surrogate recovery is still outside this range, extract and analyze one-tenth the volume of sample to overcome any matrix interference problems. If a sample is highly colored or suspected to be high in concentration, a 1-L sample aliquot and a 100-mL sample aliquot could be extracted simultaneously and still meet the holding time criteria, while providing information about a complex matrix.

16.4 Recovery of the matrix spike and matrix spike duplicate (MS/MSD)—In most samples, MS/MSD recoveries will be similar to those from reagent water. If either the MS or MSD recovery is outside the range specified in Section 8.3.3, one-tenth the volume of sample is spiked and analyzed. If the matrix spike recovery is still outside the range, the result for the unspiked sample may not be reported or used for permitting or regulatory compliance purposes. See Section 8.1.7 for dispositions of failures. Poor matrix spike recovery does not relieve a discharger or permittee of reporting timely results.

17. Method Performance

17.1 This method was tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4x MDL to 1000x MDL with the following exceptions: Chlordane recovery at 4x MDL was low (60%); Toxaphene recovery was demonstrated linear over the range of 10x MDL to 1000x MDL (Reference 3).

17.2 The 1984 version of this method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations (Reference 2). Concentrations used in the study ranged from 0.5 to 30 µg/L for single-component pesticides and from 8.5 to 400 µg/L for multi-component analytes. These data are for a subset of analytes described in the current version of the method.

17.3 During the development of Method 1656, a similar EPA procedure for the

organochlorine pesticides, single-operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 5.

18. Pollution Prevention

18.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operations. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, the laboratory should use pollution prevention techniques to address waste generation. When wastes cannot be reduced at the source, the Agency recommends recycling as the next best option.

18.2 The analytes in this method are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards. This method utilizes significant quantities of methylene chloride. Laboratories are encouraged to recover and recycle this and other solvents during extract concentration.

18.3 For information about pollution prevention that may be applied to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" (Reference 19), available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW., Washington DC 20036, 202-872-4477.

19. Waste Management

19.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. An overview of requirements can be found in Environmental Management Guide for Small Laboratories (EPA 233-B-98-001).

19.2 Samples at pH <2, or pH >12, are hazardous and must be handled and disposed of as hazardous waste, or neutralized and disposed of in accordance with all federal, state, and local regulations. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management,

see "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in section 18.3.

19.3 Many analytes in this method decompose above 500 °C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in an appropriate incinerator. Gross quantities of neat or highly concentrated solutions of toxic or hazardous chemicals should be packaged securely and disposed of through commercial or governmental channels that are capable of handling toxic wastes.

19.4 For further information on waste management, consult The Waste Management Manual for Laboratory Personnel and Less is Better-Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW., Washington, DC 20036, 202-872-4477.

20. References

1. "Determination of Pesticides and PCBs in Industrial and Municipal Wastewaters," EPA 600/4-82-023, National Technical Information Service, PB82-214222, Springfield, Virginia 22161, April 1982.
2. "EPA Method Study 18 Method 608-Organochlorine Pesticides and PCBs," EPA 600/4-84-061, National Technical Information Service, PB84-211358, Springfield, Virginia 22161, June 1984.
3. "Method Detection Limit and Analytical Curve Studies, EPA Methods 606, 607, and 608," Special letter report for EPA Contract 68-03-2606, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, June 1980.
4. ASTM Annual Book of Standards, Part 31, D3694-78. "Standard Practice for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.
5. Giam, C.S., Chan, H.S., and Nef, G.S. "Sensitive Method for Determination of Phthalate Ester Plasticizers in Open-Ocean Biota Samples," Analytical Chemistry, 47:2225 (1975).
6. Giam, C.S. and Chan, H.S. "Control of Blanks in the Analysis of Phthalates in Air and Ocean Biota Samples," U.S. National Bureau of Standards, Special Publication 442, pp. 701-708, 1976.
7. Solutions to Analytical Chemistry Problems with Clean Water Act Methods, EPA 821-R-07-002, March 2007.
8. "Carcinogens-Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.
9. "Occupational Exposure to Hazardous Chemicals in Laboratories," (29 CFR 1910.1450), Occupational Safety and Health Administration, OSHA.
10. 40 CFR 136.6(b)(4)(j).
11. Mills, P.A. "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing

- Florisil Columns,” Journal of the Association of Official Analytical Chemists, 51:29, (1968).
12. 40 CFR 136.6(b)(2)(i).
13. Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water (EPA-821-B-98-003) March 1999.
14. Methods 4500 Cl F and 4500 Cl G, Standard Methods for the Examination of Water and Wastewater, published jointly by the American Public Health Association, American Water Works Association, and Water Environment Federation, 1015 Fifteenth St., Washington, DC 20005, 20th Edition, 2000.
15. “Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples,” EPA-600/8-80-038, U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina.
16. USEPA, 2000, Method 1656 Organo-Halide Pesticides In Wastewater, Soil, Sludge, Sediment, and Tissue by GC/HSD, EPA-821-R-00-017, September 2000.
17. USEPA, 2010, Method 1668C Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, EPA-820-R-10-005, April 2010.
18. USEPA, 2007, Method 1699: Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, EPA-821-R-08-001, December 2007.
19. “Less is Better,” American Chemical Society on-line publication, <http://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/less-is-better.pdf>.
20. EPA Method 608 ATP 3M0222, An alternative test procedure for the measurement of organochlorine pesticides and polychlorinated biphenyls in waste water. **Federal Register**, Vol. 60, No. 148 August 2, 1995.
21. Tables

TABLE 1—PESTICIDES ¹

Analyte	CAS No.	MDL ² (ng/L)	ML ³ (ng/L)
Aldrin	309-00-2	4	12
alpha-BHC	319-84-6	3	9
beta-BHC	319-85-7	6	18
delta-BHC	319-86-8	9	27
gamma-BHC (Lindane)	58-89-9	4	12
alpha-Chlordane ⁴	5103-71-9	14	42
gamma-Chlordane ⁴	5103-74-2	14	42
4,4'-DDD	72-54-8	11	33
4,4'-DDE	72-55-9	4	12
4,4'-DDT	50-29-3	12	36
Dieldrin	60-57-1	2	6
Endosulfan I	959-98-8	14	42
Endosulfan II	33213-65-9	4	12
Endosulfan sulfate	1031-07-8	66	198
Endrin	72-20-8	6	18
Endrin aldehyde	7421-93-4	23	70
Heptachlor	76-44-8	3	9
Heptachlor epoxide	1024-57-3	83	249

¹ All analytes in this table are Priority Pollutants (40 CFR part 423, appendix A).

² 40 CFR part 136, appendix B, June 30, 1986.

³ ML = Minimum Level—see Glossary for definition and derivation, calculated as 3 times the MDL.

⁴ MDL based on the MDL for Chlordane.

TABLE 2—ADDITIONAL ANALYTES

Analyte	CAS No.	MDL ³ (ng/L)	ML ⁴ (ng/L)
Acephate	30560-19-1
Alachlor	15972-60-8
Atrazine	1912-24-9
Benfluralin (Benefin)	1861-40-1
Bromacil	314-40-9
Bromoxynil octanoate	1689-99-2
Butachlor	23184-66-9
Captafol	2425-06-1
Captan	133-06-2
Carbophenothion (Trithion)	786-19-6
Chlorobenzilate	510-15-6
Chloroneb (Terraneb)	2675-77-6
Chloropropylate (Acaralate)	5836-10-2
Chlorothalonil	1897-45-6
Cyanazine	21725-46-2
DCPA (Dacthal)	1861-32-1
2,4'-DDD	53-19-0
2,4'-DDE	3424-82-6
2,4'-DDT	789-02-6
Diallate (Avadex)	2303-16-4
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8
Dichlone	117-80-6
Dichloran	99-30-9
Dicofol	115-32-2

TABLE 2—ADDITIONAL ANALYTES—Continued

Analyte	CAS No.	MDL ³ (ng/L)	ML ⁴ (ng/L)
Endrin ketone	53494-70-5
Ethalfuralin (Sonalan)	55283-68-6
Etridiazole	2593-15-9
Fenarimol (Rubigan)	60168-88-9
Hexachlorobenzene ¹	118-74-1
Hexachlorocyclopentadiene ¹	77-47-4
Isodrin	465-73-6
Isopropalin (Paarlan)	33820-53-0
Kepone	143-50-0
Methoxychlor	72-43-5
Metolachlor	51218-45-2
Metribuzin	21087-64-9
Mirex	2385-85-5
Nitrofen (TOK)	1836-75-5
<i>cis</i> -Nonachlor	5103-73-1
<i>trans</i> -Nonachlor	39765-80-5
Norfluorazon	27314-13-2
Octachlorostyrene	29082-74-4
Oxychlordane	27304-13-8
PCNB (Pentachloronitrobenzene)	82-68-8
Pendamethalin (Prowl)	40487-42-1
<i>cis</i> -Permethrin	61949-76-6
<i>trans</i> -Permethrin	61949-77-7
Perthane (Ethylan)	72-56-0
Propachlor	1918-16-7
Propanil	709-98-8
Propazine	139-40-2
Quintozene	82-68-8
Simazine	122-34-9
Strobane	8001-50-1
Technazene	117-18-0
Technical Chlordane ²
Terbacil	5902-51-2
Terbuthylazine	5915-41-3
Toxaphene ¹	8001-35-2	240	720
Trifluralin	1582-09-8
PCB-1016 ¹	12674-11-2
PCB-1221 ¹	11104-28-2
PCB-1232 ¹	11141-16-5
PCB-1242 ¹	53469-21-9	65	95
PCB-1248 ¹	12672-29-6
PCB-1254 ¹	11097-69-1
PCB-1260 ¹	11096-82-5
PCB-1268	11100-14-4

¹ Priority Pollutants (40 CFR part 423, appendix A).² Technical Chlordane may be used in cases where historical reporting has only been for this form of Chlordane.³ 40 CFR part 136, appendix B, June 30, 1986.⁴ ML = Minimum Level—see Glossary for definition and derivation, calculated as 3 times the MDL.TABLE 3—EXAMPLE RETENTION TIMES ¹

Analyte	Retention time (min) ²	
	DB-608	DB-1701
Acephate	5.03	(³)
Trifluralin	5.16	6.79
Ethalfuralin	5.28	6.49
Benfluralin	5.53	6.87
Diallate-A	7.15	6.23
Diallate-B	7.42	6.77
<i>alpha</i> -BHC	8.14	7.44
PCNB	9.03	7.58
Simazine	9.06	9.29
Atrazine	9.12	9.12
Terbuthylazine	9.17	9.46
<i>gamma</i> -BHC (Lindane)	9.52	9.91
<i>beta</i> -BHC	9.86	11.90
Heptachlor	10.66	10.55
Chlorothalonil	10.66	10.96

TABLE 3—EXAMPLE RETENTION TIMES¹—Continued

Analyte	Retention time (min) ²	
	DB-608	DB-1701
Dichlone	10.80	(⁴)
Terbacil	11.11	12.63
<i>delta</i> -BHC	11.20	12.98
Alachlor	11.57	11.06
Propanil	11.60	14.10
Aldrin	11.84	11.46
DCPA	12.18	12.09
Metribuzin	12.80	11.68
Triadimefon	12.99	13.57
Isopropalin	13.06	13.37
Isodrin	13.47	11.12
Heptachlor epoxide	13.97	12.56
Pendameethalin	14.21	13.46
Bromacil	14.39	(³)
<i>alpha</i> -Chlordane	14.63	14.20
Butachlor	15.03	15.69
<i>gamma</i> -Chlordane	15.24	14.36
Endosulfan I	15.25	13.87
4,4'-DDE	16.34	14.84
Dieldrin	16.41	15.25
Captan	16.83	15.43
Chlorobenzilate	17.58	17.28
Endrin	17.80	15.86
Nitrofen (TOK)	17.86	17.47
Kepone	17.92	(^{3,5})
4,4'-DDD	18.43	17.77
Endosulfan II	18.45	18.57
Bromoxynil octanoate	18.85	18.57
4,4'-DDT	19.48	18.32
Carbophenothion	19.65	18.21
Endrin aldehyde	19.72	19.18
Endosulfan sulfate	20.21	20.37
Captafol	22.51	21.22
Norfluorazon	20.68	22.01
Mirex	22.75	19.79
Methoxychlor	22.80	20.68
Endrin ketone	23.00	21.79
Fenarimol	24.53	23.79
<i>cis</i> -Permethrin	25.00	23.59
<i>trans</i> -Permethrin	25.62	23.92
PCB-1016		
PCB-1221		
PCB-1232		
PCB-1242		
PCB-1248		
PCB-1254		
PCB-1260 (5 peaks)	15.44	14.64
	15.73	15.36
	16.94	16.53
	17.28	18.70
	19.17	19.92
Toxaphene (5 peaks)	16.60	16.60
	17.37	17.52
	18.11	17.92
	19.46	18.73
	19.69	19.00

¹ Data from EPA Method 1656 (Reference 16).² Columns: 30-m long x 0.53-mm ID fused-silica capillary; DB-608, 0.83 μ m; and DB-1701, 1.0 μ m.Conditions suggested to meet retention times shown: 150 °C for 0.5 minute, 150–270 °C at 5 °C/min, and 270 °C until *trans*-Permethrin elutes. Carrier gas flow rates approximately 7 mL/min.³ Does not elute from DB-1701 column at level tested.⁴ Not recovered from water at the levels tested.⁵ Dichlone and Kepone do not elute from the DB-1701 column and should be confirmed on DB-5.

TABLE 4—QC ACCEPTANCE CRITERIA

Analyte	Calibration verification (%)	Test concentration (µg/L)	Limit for s (% SD)	Range for \bar{X} (%)	Range for P (%)	Maximum MS/MSD RPD (%)
Aldrin	75–125	2.0	25	54–130	42–140	35
<i>alpha</i> -BHC	69–125	2.0	28	49–130	37–140	36
<i>beta</i> -BHC	75–125	2.0	38	39–130	17–147	44
<i>delta</i> -BHC	75–125	2.0	43	51–130	19–140	52
<i>gamma</i> -BHC	75–125	2.0	29	43–130	32–140	39
<i>alpha</i> -Chlordane	73–125	50.0	24	55–130	45–140	35
<i>gamma</i> -Chlordane	75–125	50.0	24	55–130	45–140	35
4,4'-DDD	75–125	10.0	32	48–130	31–141	39
4,4'-DDE	75–125	2.0	30	54–130	30–145	35
4,4'-DDT	75–125	10.0	39	46–137	25–160	42
Dieldrin	48–125	2.0	42	58–130	36–146	49
Endosulfan I	75–125	2.0	25	57–141	45–153	28
Endosulfan II	75–125	10.0	63	22–171	D–202	53
Endosulfan sulfate	70–125	10.0	32	38–132	26–144	38
Endrin	5–125	10.0	42	51–130	30–147	48
Heptachlor	75–125	2.0	28	43–130	34–140	43
Heptachlor epoxide	75–125	2.0	22	57–132	37–142	26
Toxaphene	68–134	50.0	30	56–130	41–140	41
PCB–1016	75–125	50.0	24	61–103	50–140	36
PCB–1221	75–125	50.0	50	44–150	15–178	48
PCB–1232	75–125	50.0	32	28–197	10–215	25
PCB–1242	75–125	50.0	26	50–139	39–150	29
PCB–1248	75–125	50.0	32	58–140	38–158	35
PCB–1254	75–125	50.0	34	44–130	29–140	45
PCB–1260	75–125	50.0	28	37–130	8–140	38

S = Standard deviation of four recovery measurements for the DOC (section 8.2.4).

\bar{X} = Average of four recovery measurements for the DOC (section 8.2.4).

P = Recovery for the LCS (section 8.4.3).

Note: These criteria were developed from data in Table 5 (Reference 2). Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those in Table 5.

TABLE 5—PRECISION AND RECOVERY AS FUNCTIONS OF CONCENTRATION

Analyte	Recovery, X' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Aldrin	$0.81C + 0.04$	$0.16(\bar{X}) - 0.04$	$0.20(\bar{X}) - 0.01$
<i>alpha</i> -BHC	$0.84C + 0.03$	$0.13(\bar{X}) + 0.04$	$0.23(\bar{X}) - 0.00$
<i>beta</i> -BHC	$0.81C + 0.07$	$0.22(\bar{X}) - 0.02$	$0.33(\bar{X}) - 0.05$
<i>delta</i> -BHC	$0.81C + 0.07$	$0.18(\bar{X}) + 0.09$	$0.25(\bar{X}) + 0.03$
<i>gamma</i> -BHC (Lindane)	$0.82C - 0.05$	$0.12(\bar{X}) + 0.06$	$0.22(\bar{X}) + 0.04$
Chlordane	$0.82C - 0.04$	$0.13(\bar{X}) + 0.13$	$0.18(\bar{X}) + 0.18$
4,4'-DDD	$0.84C + 0.30$	$0.20(\bar{X}) - 0.18$	$0.27(\bar{X}) - 0.14$
4,4'-DDE	$0.85C + 0.14$	$0.13(\bar{X}) + 0.06$	$0.28(\bar{X}) - 0.09$
4,4'-DDT	$0.93C - 0.13$	$0.17(\bar{X}) + 0.39$	$0.31(\bar{X}) - 0.21$
Dieldrin	$0.90C + 0.02$	$0.12(\bar{X}) + 0.19$	$0.16(\bar{X}) + 0.16$
Endosulfan I	$0.97C + 0.04$	$0.10(\bar{X}) + 0.07$	$0.18(\bar{X}) + 0.08$
Endosulfan II	$0.93C + 0.34$	$0.41(\bar{X}) - 0.65$	$0.47(\bar{X}) - 0.20$
Endosulfan sulfate	$0.89C - 0.37$	$0.13(\bar{X}) + 0.33$	$0.24(\bar{X}) + 0.35$
Endrin	$0.89C - 0.04$	$0.20(\bar{X}) + 0.25$	$0.24(\bar{X}) + 0.25$
Heptachlor	$0.69C + 0.04$	$0.06(\bar{X}) + 0.13$	$0.16(\bar{X}) + 0.08$
Heptachlor epoxide	$0.89C + 0.10$	$0.18(\bar{X}) - 0.11$	$0.25(\bar{X}) - 0.08$
Toxaphene	$0.80C + 1.74$	$0.09(\bar{X}) + 3.20$	$0.20(\bar{X}) + 0.22$
PCB–1016	$0.81C + 0.50$	$0.13(\bar{X}) + 0.15$	$0.15(\bar{X}) + 0.45$
PCB–1221	$0.96C + 0.65$	$0.29(\bar{X}) - 0.76$	$0.35(\bar{X}) - 0.62$
PCB–1232	$0.91C + 10.8$	$0.21(\bar{X}) - 1.93$	$0.31(\bar{X}) + 3.50$
PCB–1242	$0.93C + 0.70$	$0.11(\bar{X}) + 1.40$	$0.21(\bar{X}) + 1.52$
PCB–1248	$0.97C + 1.06$	$0.17(\bar{X}) + 0.41$	$0.25(\bar{X}) - 0.37$
PCB–1254	$0.76C + 2.07$	$0.15(\bar{X}) + 1.66$	$0.17(\bar{X}) + 3.62$
PCB–1260	$0.66C + 3.76$	$0.22(\bar{X}) - 2.37$	$0.39(\bar{X}) - 4.86$

X' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

TABLE 6—DISTRIBUTION OF CHLORINATED PESTICIDES AND PCBs INTO FLORISIL® COLUMN FRACTIONS

Analyte	Percent Recovery by Fraction ¹		
	1	2	3
Aldrin	100
<i>alpha</i> -BHC	100
<i>beta</i> -BHC	97
<i>delta</i> -BHC	98
<i>gamma</i> -BHC (Lindane)	100
Chlordane	100
4,4'-DDD	99
4,4'-DDE	98
4,4'-DDT	100
Dieldrin	0	100
Endosulfan I	37	64
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96
Endrin aldehyde	0	68	26
Heptachlor	100
Heptachlor epoxide	100
Toxaphene	96
PCB-1016	97
PCB-1221	97
PCB-1232	95	4
PCB-1242	97
PCB-1248	103
PCB-1254	90
PCB-1260

¹ Eluant composition:

Fraction 1—6% ethyl ether in hexane.

Fraction 2—15% ethyl ether in hexane.

Fraction 3—50% ethyl ether in hexane.

TABLE 7—SUGGESTED CALIBRATION GROUPS ¹

Analyte
<i>Calibration Group 1:</i>
Acephate
Alachlor
Atrazine
<i>beta</i> -BHC
Bromoxynil octanoate
Captafol
Diallate
Endosulfan sulfate
Endrin
Isodrin
Pendimethalin (Prowl)
<i>trans</i> -Permethrin
<i>Calibration Group 2:</i>
<i>alpha</i> -BHC
DCPA
4,4'-DDE
4,4'-DDT
Dichlone
Ethalfuralin
Fenarimol
Methoxychlor
Metribuzin
<i>Calibration Group 3:</i>
<i>gamma</i> -BHC (Lindane)
<i>gamma</i> -Chlordane

TABLE 7—SUGGESTED CALIBRATION GROUPS ¹—Continued

Analyte
Endrin ketone
Heptachlor epoxide
Isopropalin
Nitrofen (TOK)
PCNB
<i>cis</i> -Permethrin
Trifluralin
<i>Calibration Group 4:</i>
Benfluralin
Chlorobenzilate
Dieldrin
Endosulfan I
Mirex
Terbacil
Terbutylazine
Triadimefon
<i>Calibration Group 5:</i>
<i>alpha</i> -Chlordane
Captan
Chlorothalonil
4,4'-DDD
Norfluorazon
Simazine
<i>Calibration Group 6:</i>
Aldrin
<i>delta</i> -BHC

TABLE 7—SUGGESTED CALIBRATION GROUPS ¹—Continued

Analyte
Bromacil
Butachlor
Endosulfan II
Heptachlor
Kepone
<i>Calibration Group 7:</i>
Carbophenothion
Chloroneb
Chloropropylate
DBCP
Dicofol
Endrin aldehyde
Etridiazone
Perthane
Propachlor
Propanil
Propazine

¹ The analytes may be organized in other calibration groups, provided that there are no coelution problems and that all QC requirements are met.

22. Figures

BILLING CODE 6560-50-P

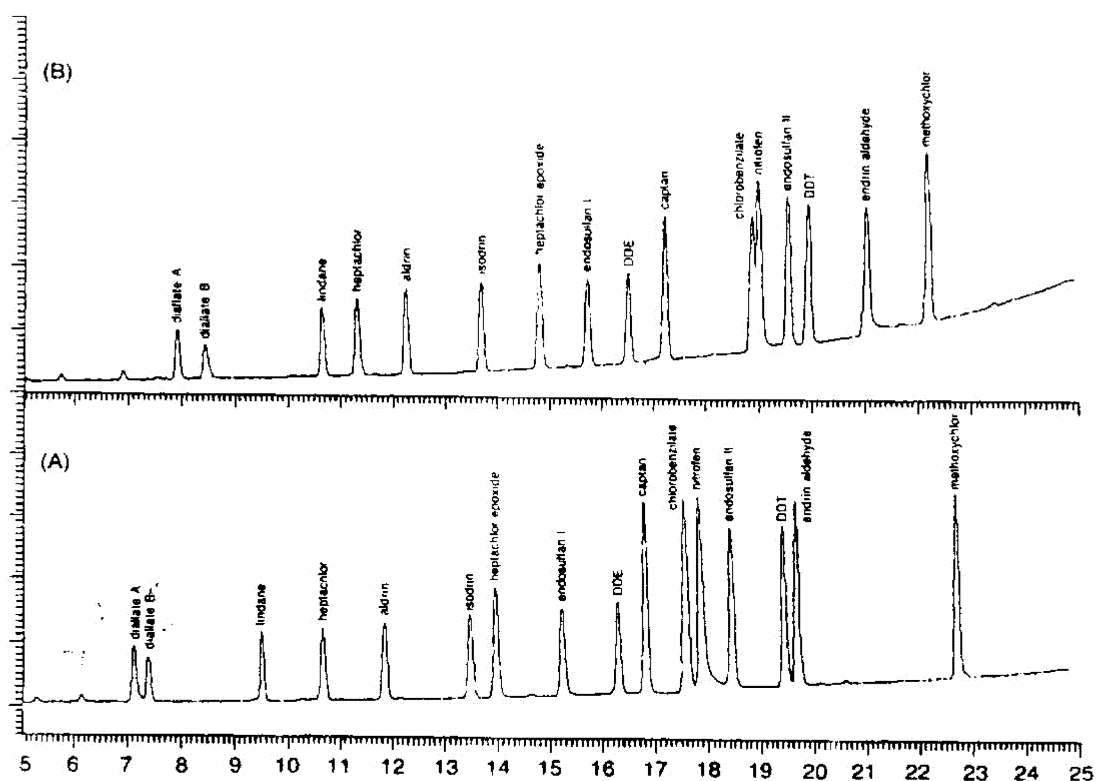


Figure 1 Example Chromatogram of Selected Organochlorine Pesticides

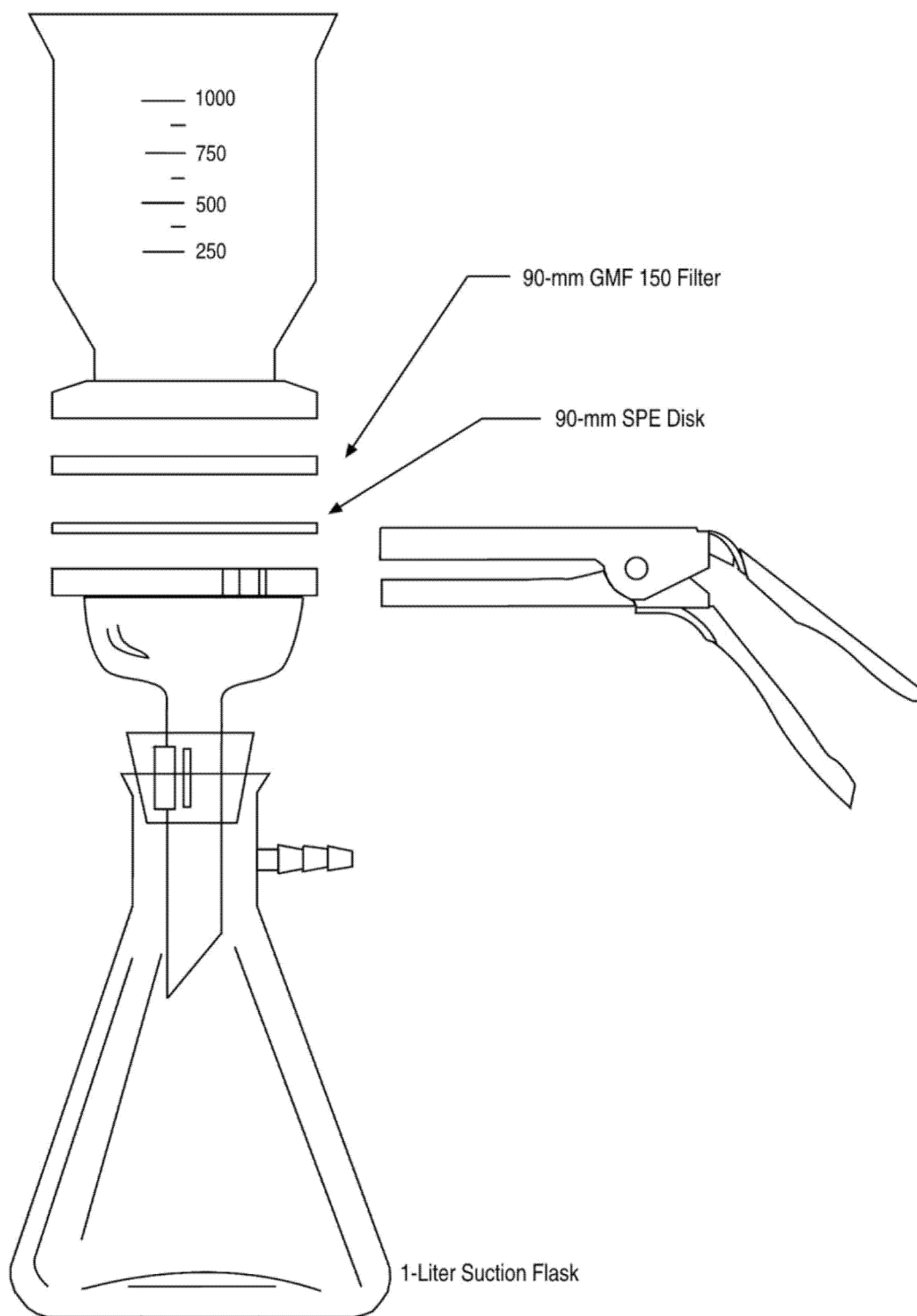


Figure 2 Disk-based solid-phase extraction apparatus

BILLING CODE 6560-50-C

23. Glossary

These definitions and purposes are specific to this method but have been conformed to common usage to the extent possible.

23.1 Units of weight and measure and their abbreviations.

23.1.1 Symbols.

°C	degrees Celsius
μg	microgram
μL	microliter
<	less than
≤	less than or equal to
>	greater than

% percent

23.1.2 Abbreviations (in alphabetical order).

cm	centimeter
g	gram
hr	hour
ID	inside diameter

in. inch

L liter

M molar solution—one mole or gram molecular weight of solute in one liter of solution

mg milligram

min minute

mL milliliter

mm millimeter

N Normality—one equivalent of solute in one liter of solution

ng nanogram

psia pounds-per-square inch absolute

psig pounds-per-square inch gauge

v/v volume per unit volume

w/v weight per unit volume

23.2 Definitions and acronyms (in alphabetical order)

Analyte—A compound or mixture of compounds (e.g., PCBs) tested for by this method. The analytes are listed in Tables 1 and 2.

Analytical batch—The set of samples analyzed on a given instrument during a 24-hour period that begins and ends with calibration verification (sections 7.8 and 13). See also “Extraction batch.”

Blank (method blank; laboratory blank)—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Calibration factor (CF)—See section 7.5.1.

Calibration standard—A solution prepared from stock solutions and/or a secondary standards and containing the analytes of interest, surrogates, and internal standards. This standard is used to model the response of the GC instrument against analyte concentration.

Calibration verification—The process of confirming that the response of the analytical system remains within specified limits of the calibration.

Calibration verification standard—The standard (section 6.8.4) used to verify calibration (sections 7.8 and 13.6).

Extraction Batch—A set of up to 20 field samples (not including QC samples) started through the extraction process in a given 24-hour shift. Each extraction batch of 20 or fewer samples must be accompanied by a blank (section 8.5), a laboratory control sample (LCS, section 8.4), a matrix spike and duplicate (MS/MSD; section 8.3), resulting in a minimum of five samples (1 field sample, 1 blank, 1 LCS, 1 MS, and 1 MSD) and a maximum of 24 samples (20 field samples, 1 blank, 1 LCS, 1 MS, and 1 MSD) for the batch. If greater than 20 samples are to be extracted in a 24-hour shift, the samples must be separated into extraction batches of 20 or fewer samples.

Field Duplicates—Two samples collected at the same time and place under identical conditions, and treated identically throughout field and laboratory procedures. Results of analyses the field duplicates provide an estimate of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Field blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample. See also “Blank.”

GC—Gas chromatograph or gas chromatography.

Gel-permeation chromatography (GPC)—A form of liquid chromatography in which the analytes are separated based on exclusion from the solid phase by size.

Internal standard—A compound added to an extract or standard solution in a known amount and used as a reference for quantitation of the analytes of interest and surrogates. Also see Internal standard quantitation.

Internal standard quantitation—A means of determining the concentration of an analyte of interest (Tables 1 and 2) by reference to a compound not expected to be found in a sample.

IDC—Initial Demonstration of Capability (section 8.2); four aliquots of a reference matrix spiked with the analytes of interest and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. An IDC is performed prior to the first time this method is used and any time the method or instrumentation is modified.

Laboratory Control Sample (LCS; laboratory fortified blank; section 8.4)—An aliquot of reagent water spiked with known quantities of the analytes of interest and surrogates. The LCS is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

Laboratory Fortified Sample Matrix—See Matrix spike.

Laboratory reagent blank—See blank.

Matrix spike (MS) and matrix spike duplicate (MSD) (laboratory fortified sample matrix and duplicate)—Two aliquots of an environmental sample to which known quantities of the analytes of interest and surrogates are added in the laboratory. The MS/MSD are prepared and analyzed exactly like a field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

May—This action, activity, or procedural step is neither required nor prohibited.

May not—This action, activity, or procedural step is prohibited.

Method detection limit (MDL)—A detection limit determined by the procedure at 40 CFR part 136, appendix B. The MDLs determined by EPA are listed in Tables 1 and 2. As noted in section 1.6, use the MDLs in Tables 1 and 2 in conjunction with current MDL data from the laboratory actually analyzing samples to assess the sensitivity of this procedure relative to project objectives

and regulatory requirements (where applicable).

Minimum level (ML)—The term “minimum level” refers to either the sample concentration equivalent to the lowest calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher. Minimum levels may be obtained in several ways: They may be published in a method; they may be based on the lowest acceptable calibration point used by a laboratory; or they may be calculated by multiplying the MDL in a method, or the MDL determined by a laboratory, by a factor of 3. For the purposes of NPDES compliance monitoring, EPA considers the following terms to be synonymous: “quantitation limit,” “reporting limit,” and “minimum level.”

MS—Mass spectrometer or mass spectrometry.

Must—This action, activity, or procedural step is required.

Preparation blank—See blank.

Reagent water—Water demonstrated to be free from the analytes of interest and potentially interfering substances at the MDLs for the analytes in this method.

Regulatory compliance limit—A limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory/control authority.

Relative standard deviation (RSD)—The standard deviation times 100 divided by the mean. Also termed “coefficient of variation.”

RF—Response factor. See section 7.6.2.

RPD—Relative percent difference.

RSD—See relative standard deviation.

Safety Data Sheet (SDS)—Written information on a chemical’s toxicity, health hazards, physical properties, fire, and reactivity, including storage, spill, and handling precautions that meet the requirements of OSHA, 29 CFR 1910.1200(g) and appendix D to § 1910.1200. United Nations Globally Harmonized System of Classification and Labelling of Chemicals (GHS), third revised edition, United Nations, 2009.

Should—This action, activity, or procedural step is suggested but not required.

SPE—Solid-phase extraction; a sample extraction or extract cleanup technique in which an analyte is selectively removed from a sample or extract by passage over or through a material capable of reversibly adsorbing the analyte.

Stock solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

Surrogate—A compound unlikely to be found in a sample, which is spiked into the sample in a known amount before extraction, and which is quantified with the same procedures used to quantify other sample components. The purpose of the surrogate is to monitor method performance with each sample.

* * * * *

Method 611—Haloethers

1. Scope and Application

1.1 This method covers the determination of certain haloethers. The following

parameters can be determined by this method:

Parameter	STORET No.	CAS No.
Bis(2-chloroethyl) ether	34273	111-44-4
Bis(2-chloroethoxy) methane	34278	111-91-1
2, 2'-oxybis (1-chloropropane)	34283	108-60-1
4-Bromophenyl phenyl ether	34636	101-55-3
4-Chlorophenyl phenyl ether	34641	7005-72-3

* * * * *

Method 624.1—Purgeables by GC/MS

1. Scope and Application

1.1 This method is for determination of purgeable organic pollutants in industrial discharges and other environmental samples by gas chromatography combined with mass spectrometry (GC/MS), as provided under 40 CFR 136.1. This revision is based on previous protocols (References 1–3), on the revision promulgated October 26, 1984, and on an interlaboratory method validation study (Reference 4). Although this method was validated through an interlaboratory study conducted in the early 1980s, the fundamental chemistry principles used in this method remain sound and continue to apply.

1.2 The analytes that may be qualitatively and quantitatively determined using this method and their CAS Registry numbers are listed in Table 1. The method may be extended to determine the analytes listed in Table 2; however, poor purging efficiency or gas chromatography of some of these analytes may make quantitative determination difficult. For example, an elevated temperature may be required to purge some analytes from water. If an elevated temperature is used, calibration and all quality control (QC) tests must be performed at the elevated temperature. EPA encourages the use of this method to determine additional compounds amenable to purge-and-trap GC/MS.

1.3 The large number of analytes in Tables 1 and 2 of this method makes testing difficult if all analytes are determined simultaneously. Therefore, it is necessary to determine and perform QC tests for “analytes of interest” only. Analytes of interest are those required to be determined by a regulatory/control authority or in a permit, or by a client. If a list of analytes is not specified, the analytes in Table 1 must be determined, at a minimum, and QC testing must be performed for these analytes. The analytes in Table 1 and some of the analytes in Table 2 have been identified as Toxic Pollutants (40 CFR 401.15), expanded to a list of Priority Pollutants (40 CFR part 423, appendix A).

1.4 Method detection limits (MDLs; Reference 5) for the analytes in Table 1 are listed in that table. These MDLs were determined in reagent water (Reference 6). Advances in analytical technology, particularly the use of capillary (open-tubular) columns, allowed laboratories to routinely achieve MDLs for the analytes in

this method that are 2–10 times lower than those in the version promulgated in 1984. The MDL for a specific wastewater may differ from those listed, depending on the nature of interferences in the sample matrix.

1.4.1 EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described in section 13.2 are focused on such monitoring needs and may not be relevant to other uses of the method.

1.4.2 This method includes “reporting limits” based on EPA’s “minimum level” (ML) concept (see the glossary in section 20). Table 1 contains MDL values and ML values for many of the analytes. The MDL for an analyte in a specific wastewater may differ from that listed in Table 1, depending upon the nature of interferences in the sample matrix.

1.5 This method is performance-based. It may be modified to improve performance (e.g., to overcome interferences or improve the accuracy of results) provided all performance requirements are met.

1.5.1 Examples of allowed method modifications are described at 40 CFR 136.6. Other examples of allowed modifications specific to this method are described in section 8.1.2.

1.5.2 Any modification beyond those expressly allowed at 40 CFR 136.6 or in section 8.1.2 of this method shall be considered a major modification that is subject to application and approval of an alternate test procedure under 40 CFR 136.4 and 136.5.

1.5.3 For regulatory compliance, any modification must be demonstrated to produce results equivalent or superior to results produced by this method when applied to relevant wastewaters (section 8.3).

1.6 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge-and-trap system and a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure in section 8.2.

1.7 Terms and units of measure used in this method are given in the glossary at the end of the method.

2. Summary of Method

2.1 A gas is bubbled through a measured volume of water in a specially-designed purging chamber. The purgeables are

efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the gas to desorb the purgeables onto a gas chromatographic column. The column is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

2.2 Different sample sizes in the range of 5–25 mL are allowed in order to meet differing sensitivity requirements. Calibration and QC samples must have the same volume as field samples.

3. Interferences

3.1 Impurities in the purge gas, organic compounds outgassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing blanks initially and with each analytical batch (samples analyzed on a given 12-hour shift, to a maximum of 20 samples), as described in Section 8.5. Fluoropolymer tubing, fittings, and thread sealant should be used to avoid contamination.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. Protect samples from sources of volatiles during collection, shipment, and storage. A reagent water field blank carried through sampling and analysis can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are analyzed sequentially. To reduce the potential for carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a blank to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105 °C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required. Screening samples at high dilution may prevent introduction of contaminants into the system.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDSs, OSHA, 29 CFR 1910.1200(g)) should also be made available to all personnel involved in sample handling and chemical analysis. Additional references to laboratory safety are available and have been identified (References 7–9) for the information of the analyst.

4.2. The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: Benzene; carbon tetrachloride; chloroform; 1,4-dichlorobenzene; 1,2-dichloroethane; 1,2-dichloropropane; methylene chloride; tetrachloroethylene; trichloroethylene; and vinyl chloride. Primary standards of these toxic compounds should be prepared in a chemical fume hood, and a NIOSH/MESA approved toxic gas respirator should be worn when handling high concentrations of these compounds.

4.3 This method allows the use of hydrogen as a carrier gas in place of helium (Section 5.3.1.2). The laboratory should take the necessary precautions in dealing with hydrogen, and should limit hydrogen flow at the source to prevent buildup of an explosive mixture of hydrogen in air.

5. Apparatus and Materials

Note: Brand names, suppliers, and part numbers are cited for illustration purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here. Demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory. Suppliers for equipment and materials in this method may be found through an on-line search.

5.1 Sampling equipment for discrete sampling.

5.1.1 Vial—25- or 40-mL capacity, or larger, with screw cap with a hole in the center (Fisher #13075 or equivalent). Unless pre-cleaned, detergent wash, rinse with tap and reagent water, and dry at 105 ± 5 °C before use.

5.1.2 Septum—Fluoropolymer-faced silicone (Fisher #12722 or equivalent). Unless pre-cleaned, detergent wash, rinse with tap and reagent water, and dry at 105 ± 5 °C for one hour before use.

5.2 Purge-and-trap system—The purge-and-trap system consists of three separate pieces of equipment: A purging device, trap, and desorber. Several complete systems are commercially available with autosamplers. Any system that meets the performance requirements in this method may be used.

5.2.1 The purging device should accept 5- to 25-mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided

bubbles. The purge gas must be introduced no more than 5 mm from the base of the water column. Purge devices of a different volume may be used so long as the performance requirements in this method are met.

5.2.2 The trap should be at least 25 cm long and have an inside diameter of at least 0.105 in. The trap should be packed to contain the following minimum lengths of adsorbents: 1.0 cm of methyl silicone coated packing (section 6.3.2), 15 cm of 2,6-diphenylene oxide polymer (section 6.3.1), and 8 cm of silica gel (section 6.3.3). A trap with different dimensions and packing materials is acceptable so long as the performance requirements in this method are met.

5.2.3 The desorber should be capable of rapidly heating the trap to the temperature necessary to desorb the analytes of interest, and of maintaining this temperature during desorption. The trap should not be heated higher than the maximum temperature recommended by the manufacturer.

5.2.4 The purge-and-trap system may be assembled as a separate unit or coupled to a gas chromatograph.

5.3 GC/MS system.

5.3.1 Gas chromatograph (GC)—An analytical system complete with a temperature programmable gas chromatograph and all required accessories, including syringes and analytical columns. Autosamplers designed for purge-and-trap analysis of volatiles also may be used.

5.3.1.1 Injection port—Volatiles interface, split, splitless, temperature programmable split/splitless (PTV), large volume, on-column, backflushed, or other.

5.3.1.2 Carrier gas—Data in the tables in this method were obtained using helium carrier gas. If another carrier gas is used, analytical conditions may need to be adjusted for optimum performance, and calibration and all QC tests must be performed with the alternative carrier gas. See Section 4.3 for precautions regarding the use of hydrogen as a carrier gas.

5.3.2 GC column—See the footnote to Table 3. Other columns or column systems may be used provided all requirements in this method are met.

5.3.3 Mass spectrometer—Capable of repetitively scanning from 35–260 Daltons (amu) every 2 seconds or less, utilizing a 70 eV (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all criteria in Table 4 when 50 ng or less of 4-bromofluorobenzene (BFB) is injected through the GC inlet. If acrolein, acrylonitrile, chloromethane, and vinyl chloride are to be determined, it may be necessary to scan from below 25 Daltons to measure the peaks in the 26–35 Dalton range for reliable identification.

5.3.4 GC/MS interface—Any GC to MS interface that meets all performance requirements in this method may be used.

5.3.5 Data system—A computer system must be interfaced to the mass spectrometer that allows continuous acquisition and storage of mass spectra throughout the chromatographic program. The computer must have software that allows searching any

GC/MS data file for specific m/z's (masses) and plotting m/z abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must also be available that allows integrating the abundance at any EICP between specified time or scan number limits.

5.4 Syringes—Graduated, 5–25 mL, glass hypodermic with Luerlok tip, compatible with the purging device.

5.5 Micro syringes—Graduated, 25–1000 µL, with 0.006 in. ID needle.

5.6 Syringe valve—Two-way, with Luer ends.

5.7 Syringe—5 mL, gas-tight with shut-off valve.

5.8 Bottle—15 mL, screw-cap, with Teflon cap liner.

5.9 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as water in which the analytes of interest and interfering compounds are not detected at the MDLs of the analytes of interest. It may be generated by passing deionized water, distilled water, or tap water through a carbon bed, passing the water through a water purifier, or heating the water to between 90 and 100 °C while bubbling contaminant-free gas through it for approximately 1 hour. While still hot, transfer the water to screw-cap bottles and seal with a fluoropolymer-lined cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Trap materials.

6.3.1 2,6-Diphenylene oxide polymer—Tenax, 60/80 mesh, chromatographic grade, or equivalent.

6.3.2 Methyl silicone packing—3% OV-1 on Chromosorb-W, 60/80 mesh, or equivalent.

6.3.3 Silica gel—35/60 mesh, Davison, Grade-15 or equivalent.

6.3.4 Other trap materials are acceptable if performance requirements in this method are met.

6.4 Methanol—Demonstrated to be free from the target analytes and potentially interfering compounds.

6.5 Stock standard solutions—Stock standard solutions may be prepared from pure materials, or purchased as certified solutions. Traceability must be to the National Institute of Standards and Technology (NIST) or other national or international standard, when available. Stock solution concentrations alternative to those below may be used. Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because some of the compounds in this method are known to be toxic, primary dilutions should be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations of neat materials are handled. The following procedure may be used to prepare standards from neat materials:

6.5.1 Place about 9.8 mL of methanol in a 10-mL ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

6.5.2 Add the assayed reference material.

6.5.2.1 Liquids—Using a 100 μL syringe, immediately add two or more drops of assayed reference material to the flask. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask. Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in $\mu\text{g}/\mu\text{L}$ from the net gain in weight.

6.5.2.2 Gases—To prepare standards for any of compounds that boil below 30 $^{\circ}\text{C}$, fill a 5-mL valved gas-tight syringe with reference standard vapor to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the vapor above the surface of the liquid (the vapor will rapidly dissolve in the methanol). Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in $\mu\text{g}/\mu\text{L}$ from the net gain in weight.

6.5.3 When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.5.4 Prepare fresh standards weekly for the gases and 2-chloroethylvinyl ether. Unless stated otherwise in this method, store non-aqueous standards in fluoropolymer-lined screw-cap, or heat-sealed, glass containers, in the dark at -20 to -10 $^{\circ}\text{C}$. Store aqueous standards; e.g., the aqueous LCS (section 8.4.1) in the dark at ≤ 6 $^{\circ}\text{C}$ (but do not freeze) with zero headspace; e.g., in VOA vials (section 5.1.1). Standards prepared by the laboratory may be stored for up to one month, except when comparison with QC check standards indicates that a standard has degraded or become more concentrated due to evaporation, or unless the laboratory has data on file to prove stability for a longer period. Commercially prepared standards may be stored until the expiration date provided by the vendor, except when comparison with QC check standards indicates that a standard has degraded or become more concentrated due to evaporation, or unless the laboratory has data from the vendor on file to prove stability for a longer period.

Note: 2-Chloroethylvinyl ether has been shown to be stable for as long as one month if prepared as a separate standard, and the other analytes have been shown to be stable for as long as 2 months if stored at less than -10 $^{\circ}\text{C}$ with minimal headspace in sealed, miniature inert-valved vials.

6.6 Secondary dilution standards—Using stock solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed. Secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in section 7.3.2 will bracket the working range of the analytical system.

6.7 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 5. The surrogates selected should match the purging characteristics of the analytes of interest as

closely as possible. Prepare a stock standard solution for each surrogate in methanol as described in section 6.5, and prepare a solution for spiking the surrogates into all blanks, LCSs, and MS/MSDs. Prepare the spiking solution such that spiking a small volume will result in a constant concentration of the surrogates. For example, add 10 μL of a spiking solution containing the surrogates at a concentration of 15 $\mu\text{g}/\text{mL}$ in methanol to a 5-mL aliquot of water to produce a concentration of 30 $\mu\text{g}/\text{L}$ for each surrogate. Other surrogate concentrations may be used. Store per section 6.5.4.

6.8 BFB standard—Prepare a solution of BFB in methanol as described in Sections 6.5 and 6.6. The solution should be prepared such that an injection or purging from water will result in introduction of ≤ 50 ng into the GC. BFB may be included in a mixture with the internal standards and/or surrogates.

6.9 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Assemble a purge-and-trap system that meets the specifications in Section 5.2. Prior to first use, condition the trap overnight at 180 $^{\circ}\text{C}$ by backflushing with gas at a flow rate of at least 20 mL/min. Condition the trap after each analysis at a temperature and time sufficient to prevent detectable concentrations of the analytes or contaminants in successive analyses.

7.2 Connect the purge-and-trap system to the gas chromatograph. The gas chromatograph should be operated using temperature and flow rate conditions equivalent to those given in the footnotes to Table 3. Alternative temperature and flow rate conditions may be used provided that performance requirements in this method are met.

7.3 Internal standard calibration.

7.3.1 Internal standards.

7.3.1.1 Select three or more internal standards similar in chromatographic behavior to the compounds of interest. Suggested internal standards are listed in Table 5. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are found at the base peak, use one of the next two most intense m/z 's for quantitation. Demonstrate that measurements of the internal standards are not affected by method or matrix interferences.

7.3.1.2 To assure accurate analyte identification, particularly when selected ion monitoring (SIM) is used, it may be advantageous to include more internal standards than those suggested in Section 7.3.1.1. An analyte will be located most accurately if its retention time relative to an internal standard is in the range of 0.8 to 1.2.

7.3.1.3 Prepare a stock standard solution for each internal standard in methanol as described in Section 6.5, and prepare a solution for spiking the internal standards into all blanks, LCSs, and MS/MSDs. Prepare the spiking solution such that spiking a small volume will result in a constant concentration of the internal standards. For example, add 10 μL of a spiking solution containing the internal standards at a concentration of 15 $\mu\text{g}/\text{mL}$ in methanol to a 5-mL aliquot of water to produce a

concentration of 30 $\mu\text{g}/\text{L}$ for each internal standard. Other concentrations may be used. The internal standard solution and the surrogate standard spiking solution (Section 6.7) may be combined, if desired. Store per section 6.5.4.

7.3.2 Calibration.

7.3.2.1 Calibration standards.

7.3.2.1.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding appropriate volumes of one or more stock standards to a fixed volume (e.g., 40 mL) of reagent water in volumetric glassware. Fewer levels may be necessary for some analytes based on the sensitivity of the MS, but no fewer than 3 levels may be used, and only the highest or lowest point(s) may be dropped from the calibration. One of the calibration standards should be at a concentration at or below the ML or as specified by a regulatory/control authority or in a permit. The ML value may be rounded to a whole number that is more convenient for preparing the standard, but must not exceed the ML values listed in Table 1 for those analytes which list ML values. Alternatively, the laboratory may establish the ML for each analyte based on the concentration of the lowest calibration standard in a series of standards produced in the laboratory or obtained from a commercial vendor, again, provided that the ML value does not exceed the MLs in Table 1, and provided that the resulting calibration meets the acceptance criteria in Section 7.3.4, based on the RSD, RSE, or R^2 . The concentrations of the higher standards should correspond to the expected range of concentrations found in real samples, or should define the working range of the GC/MS system for full-scan and/or SIM operation, as appropriate. A minimum of six concentration levels is required for a second order, non-linear (e.g., quadratic; $ax^2 + bx + c = 0$) calibration. Calibrations higher than second order are not allowed.

7.3.2.1.2 To each calibration standard or standard mixture, add a known constant volume of the internal standard spiking solution (section 7.3.1.3) and surrogate standard spiking solution (section 6.7) or the combined internal standard solution and surrogate spiking solution (section 7.3.1.3). Aqueous standards may be stored up to 24 hours, if held in sealed vials with zero headspace. If not so stored, they must be discarded after one hour.

7.3.2.2 Prior to analysis of the calibration standards, analyze the BFB standard (section 6.8) and adjust the scan rate of the MS to produce a minimum of 5 mass spectra across the BFB GC peak, but do not exceed 2 seconds per scan. Adjust instrument conditions until the BFB criteria in Table 4 are met. Once the scan conditions are established, they must be used for analyses of all standards, blanks, and samples.

Note: The BFB spectrum may be evaluated by summing the intensities of the m/z 's across the GC peak, subtracting the background at each m/z in a region of the chromatogram within 20 scans of but not including any part of the BFB peak. The BFB spectrum may also be evaluated by fitting a Gaussian to each m/z and using the intensity

at the maximum for each Gaussian, or by integrating the area at each m/z and using the integrated areas. Other means may be used for evaluation of the BFB spectrum so long as the spectrum is not distorted to meet the criteria in Table 4.

7.3.2.3 Analyze the mid-point standard and enter or review the retention time, relative retention time, mass spectrum, and quantitation m/z in the data system for each analyte of interest, surrogate, and internal standard. If additional analytes (Table 2) are to be quantified, include these analytes in the standard. The mass spectrum for each analyte must be comprised of a minimum of 2 m/z 's; 3 to 5 m/z 's assure more reliable analyte identification. Suggested quantitation m/z 's are shown in Table 6 as the primary m/z . For analytes in Table 6 that do not have a secondary m/z , acquire a mass spectrum and enter one or more secondary m/z 's for more reliable identification. If an interference

occurs at the primary m/z , use one of the secondary m/z 's or an alternative m/z . A single m/z only is required for quantitation.

7.3.2.4 For SIM operation, determine the analytes in each descriptor, the quantitation m/z for each analyte (the quantitation m/z can be the same as for full-scan operation; Section 7.3.2.3), the dwell time on each m/z for each analyte, and the beginning and ending retention time for each descriptor. Analyze the verification standard in scan mode to verify m/z 's and establish retention times for the analytes. There must be a minimum of two m/z 's for each analyte to assure analyte identification. To maintain sensitivity, the number of m/z 's in a descriptor should be limited. For example, for a descriptor with 10 m/z 's and a chromatographic peak width of 5 sec, a dwell time of 100 ms at each m/z would result in a scan time of 1 second and provide 5 scans across the GC peak. The quantitation m/z will usually be the most intense peak in the

mass spectrum. The quantitation m/z and dwell time may be optimized for each analyte. The acquisition table used for SIM must take into account the mass defect (usually less than 0.2 Dalton) that can occur at each m/z monitored. Refer to the footnotes to Table 3 for establishing operating conditions and to section 7.3.2.2 for establishing scan conditions.

7.3.2.5 For combined scan and SIM operation, set up the scan segments and descriptors to meet requirements in sections 7.3.2.2–7.3.2.4. Analyze unfamiliar samples in the scan mode to assure that the analytes of interest are determined.

7.3.3 Analyze each calibration standard according to Section 10 and tabulate the area at the quantitation m/z against concentration for each analyte of interest, surrogate, and internal standard. Calculate the response factor (RF) for each compound at each concentration using Equation 1.

$$RF = \frac{(A_s \times C_{is})}{(A_{is} \times C_s)} \quad \text{Equation 1}$$

Where:

A_s = Area of the characteristic m/z for the analyte to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard ($\mu\text{g/L}$).

C_s = Concentration of the analyte to be measured ($\mu\text{g/L}$).

7.3.4 Calculate the mean (average) and relative standard deviation (RSD) of the response factors. If the RSD is less than 35%, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to fit a linear or quadratic regression of response ratios, A_s/A_{is} , vs. concentration ratios C_s/C_{is} . If used, the regression must be weighted inversely proportional to concentration ($1/C$). The coefficient of determination (R^2) of the weighted regression must be greater than 0.920 (this value roughly corresponds to the RSD limit of 35%). Alternatively, the relative standard error (Reference 10) may be used as an acceptance criterion. As with the RSD, the RSE must be less than 35%. If an RSE less than 35% cannot be achieved for a quadratic regression, system performance is unacceptable, and the system must be adjusted and re-calibrated.

Note: Using capillary columns and current instrumentation, it is quite likely that a laboratory can calibrate the target analytes in this method and achieve a linearity metric (either RSD or RSE) well below 35%. Therefore, laboratories are permitted to use more stringent acceptance criteria for calibration than described here, for example, to harmonize their application of this method with those from other sources.

7.4 Calibration verification—Because the analytical system is calibrated by purge of the analytes from water, calibration verification is performed using the laboratory control sample (LCS). See section 8.4 for requirements for calibration verification

using the LCS, and the Glossary for further definition.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analysis of spiked samples and blanks to evaluate and document data quality (40 CFR 136.7). The laboratory must maintain records to document the quality of data generated. Results of ongoing performance tests are compared with established QC acceptance criteria to determine if the results of analyses meet performance requirements of this method. When results of spiked samples do not meet the QC acceptance criteria in this method, a quality control check sample (laboratory control sample; LCS) must be analyzed to confirm that the measurements were performed in an in-control mode of operation. A laboratory may develop its own performance criteria (as QC acceptance criteria), provided such criteria are as or more restrictive than the criteria in this method.

8.1.1 The laboratory must make an initial demonstration of capability (DOC) to generate acceptable precision and recovery with this method. This demonstration is detailed in Section 8.2. On a continuing basis, the laboratory must repeat demonstration of capability (DOC) at least annually.

8.1.2 In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options (section 1.5 and 40 CFR 136.6(b)) to improve separations or lower the costs of measurements. These options may include an alternative purge-and-trap device, and changes in both column and type of mass spectrometer (see 40 CFR 136.6(b)(4)(xvi)). Alternative determinative techniques, such as substitution of

spectroscopic or immunoassay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than GC/MS is used, that technique must have a specificity equal to or greater than the specificity of GC/MS for the analytes of interest. The laboratory is also encouraged to participate in inter-comparison and performance evaluation studies (see section 8.8).

8.1.2.1 Each time a modification is made to this method, the laboratory is required to repeat the procedure in section 8.2. If the detection limit of the method will be affected by the change, the laboratory must demonstrate that the MDLs (40 CFR part 136, appendix B) are lower than one-third the regulatory compliance limit or the MDLs in this method, whichever are greater. If calibration will be affected by the change, the instrument must be recalibrated per section 7. Once the modification is demonstrated to produce results equivalent or superior to results produced by this method, that modification may be used routinely thereafter, so long as the other requirements in this method are met (e.g., matrix spike/matrix spike duplicate recovery and relative percent difference).

8.1.2.1.1 If a modification is to be applied to a specific discharge, the laboratory must prepare and analyze matrix spike/matrix spike duplicate (MS/MSD) samples (Section 8.3) and LCS samples (section 8.4). The laboratory must include internal standards and surrogates (section 8.7) in each of the samples. The MS/MSD and LCS samples must be fortified with the analytes of interest (section 1.3.). If the modification is for nationwide use, MS/MSD samples must be prepared from a minimum of nine different discharges (See section 8.1.2.1.2), and all QC acceptance criteria in this method must be met. This evaluation only needs to be performed once, other than for the routine QC required by this method (for example it

could be performed by the vendor of the alternative materials) but any laboratory using that specific material must have the results of the study available. This includes a full data package with the raw data that will allow an independent reviewer to verify each determination and calculation performed by the laboratory (see section 8.1.2.2.5, items (a)–(l)).

8.1.2.1.2 Sample matrices on which MS/MSD tests must be performed for nationwide use of an allowed modification:

(a) Effluent from a publicly owned treatment works (POTW).

(b) ASTM D5905 Standard Specification for Substitute Wastewater.

(c) Sewage sludge, if sewage sludge will be in the permit.

(d) ASTM D1141 Standard Specification for Substitute Ocean Water, if ocean water will be in the permit.

(e) Untreated and treated wastewaters up to a total of nine matrix types (see <https://www.epa.gov/eg/industrial-effluent-guidelines> for a list of industrial categories with existing effluent guidelines).

(i) At least one of the above wastewater matrix types must have at least one of the following characteristics:

(A) Total suspended solids greater than 40 mg/L.

(B) Total dissolved solids greater than 100 mg/L.

(C) Oil and grease greater than 20 mg/L.

(D) NaCl greater than 120 mg/L.

(E) CaCO₃ greater than 140 mg/L.

(ii) Results of MS/MSD tests must meet QC acceptance criteria in section 8.3.

(f) A proficiency testing (PT) sample from a recognized provider, in addition to tests of the nine matrices (section 8.1.2.1.1).

8.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

8.1.2.2.1 The names, titles, and business street addresses, telephone numbers, and email addresses of the analyst(s) that performed the analyses and modification, and of the quality control officer that witnessed and will verify the analyses and modifications.

8.1.2.2.2 A list of analytes, by name and CAS Registry Number.

8.1.2.2.3 A narrative stating reason(s) for the modifications.

8.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

(a) Calibration (section 7).

(b) Calibration verification/LCS (section 8.4).

(c) Initial demonstration of capability (section 8.2).

(d) Analysis of blanks (section 8.5).

(e) Matrix spike/matrix spike duplicate analysis (section 8.3).

(f) Laboratory control sample analysis (section 8.4).

8.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

(a) Sample numbers and other identifiers.

(b) Analysis dates and times.

(c) Analysis sequence/run chronology.

(d) Sample volume (Section 10).

(e) Sample dilution (Section 13.2).

(f) Instrument and operating conditions.

(g) Column (dimensions, material, etc.).

(h) Operating conditions (temperature program, flow rate, etc.).

(i) Detector (type, operating conditions, etc.).

(j) Chromatograms, mass spectra, and other recordings of raw data.

(k) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.

(l) A written Standard Operating Procedure (SOP).

8.1.2.2.6 Each individual laboratory wishing to use a given modification must perform the start-up tests in section 8.1.2 (e.g., DOC, MDL), with the modification as an integral part of this method prior to applying the modification to specific discharges. Results of the DOC must meet the QC acceptance criteria in Table 7 for the analytes of interest (section 1.3), and the MDLs must be equal to or lower than the MDLs in Table 3 for the analytes of interest.

8.1.3 Before analyzing samples, the laboratory must analyze a blank to demonstrate that interferences from the analytical system, labware, and reagents are under control. Each time a batch of samples is analyzed or reagents are changed, a blank must be analyzed as a safeguard against laboratory contamination. Requirements for the blank are given in section 8.5.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze samples to monitor and evaluate method and laboratory performance on the sample matrix. The procedure for spiking and analysis is given in section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through analysis of a quality control check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) that the measurement system is in control. This procedure is given in section 8.4.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is given in section 8.8.

8.1.7 The large number of analytes tested in performance tests in this method present a substantial probability that one or more will fail acceptance criteria when many analytes are tested simultaneously, and a re-test is allowed if this situation should occur. If, however, continued re-testing results in further repeated failures, the laboratory must document and report the failures (e.g., as qualifiers on results), unless the failures are not required to be reported as determined by the regulatory/control authority. Results associated with a QC failure for an analyte regulated in a discharge cannot be used to demonstrate regulatory compliance. QC failures do not relieve a discharger or permittee of reporting timely results.

8.2 Initial demonstration of capability (DOC)—To establish the ability to generate acceptable recovery and precision, the laboratory must perform the DOC in sections 8.2.1 through 8.2.6 for the analytes of interest. The laboratory must also establish

MDLs for the analytes of interest using the MDL procedure at 40 CFR part 136, appendix B. The laboratory's MDLs must be equal to or lower than those listed in Table 1 for those analytes which list MDL values, or lower than one-third the regulatory compliance limit, whichever is greater. For MDLs not listed in Table 1, the laboratory must determine the MDLs using the MDL procedure at 40 CFR part 136, appendix B under the same conditions used to determine the MDLs for the analytes listed in Table 1. All procedures used in the analysis must be included in the DOC.

8.2.1 For the DOC, a QC check sample concentrate (LCS concentrate) containing each analyte of interest (section 1.3) is prepared in methanol. The QC check sample concentrate must be prepared independently from those used for calibration, but may be from the same source as the second-source standard used for calibration verification/LCS (sections 7.4 and 8.4). The concentrate should produce concentrations of the analytes of interest in water at the mid-point of the calibration range, and may be at the same concentration as the LCS (section 8.4).

Note: QC check sample concentrates are no longer available from EPA.

8.2.2 Using a pipet or micro-syringe, prepare four LCSs by adding an appropriate volume of the concentrate to each of four aliquots of reagent water. The volume of reagent water must be the same as the volume that will be used for the sample, blank (section 8.5), and MS/MSD (section 8.3). A volume of 5 mL and a concentration of 20 µg/L were used to develop the QC acceptance criteria in Table 7. An alternative volume and sample concentration may be used, provided that all QC tests are performed and all QC acceptance criteria in this method are met. Also add an aliquot of the surrogate spiking solution (section 6.7) and internal standard spiking solution (section 7.3.1.3) to the reagent-water aliquots.

8.2.3 Analyze the four LCSs according to the method beginning in section 10.

8.2.4 Calculate the average percent recovery (\bar{X}) and the standard deviation of the percent recovery (s) for each analyte using the four results.

8.2.5 For each analyte, compare s and \bar{X} with the corresponding acceptance criteria for precision and recovery in Table 7. For analytes in Tables 1 and 2 not listed in Table 7, DOC QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 11 and 12). Alternatively, acceptance criteria for analytes not listed in Table 7 may be based on laboratory control charts. If s and \bar{X} for all analytes of interest meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If any individual s exceeds the precision limit or any individual \bar{X} falls outside the range for recovery, system performance is unacceptable for that analyte.

Note: The large number of analytes in Tables 1 and 2 present a substantial probability that one or more will fail at least one of the acceptance criteria when many or all analytes are determined simultaneously. Therefore, the analyst is permitted to conduct a "re-test" as described in section 8.2.6.

8.2.6 When one or more of the analytes tested fail at least one of the acceptance criteria, repeat the test for only the analytes that failed. If results for these analytes pass, system performance is acceptable and analysis of samples and blanks may proceed. If one or more of the analytes again fail, system performance is unacceptable for the analytes that failed the acceptance criteria. Correct the problem and repeat the test (section 8.2). See section 8.1.7 for disposition of repeated failures.

Note: To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between this pair of tests.

8.3 Matrix spike and matrix spike duplicate (MS/MSD)—The purpose of the MS/MSD requirement is to provide data that demonstrate the effectiveness of the method as applied to the samples in question by a given laboratory, and both the data user (discharger, permittee, regulated entity, regulatory/control authority, customer, other) and the laboratory share responsibility for provision of such data. The data user should identify the sample and the analytes of interest (section 1.3) to be spiked and provide sufficient sample volume to perform MS/MSD analyses. The laboratory must, on an ongoing basis, spike at least 5% of the samples in duplicate from each discharge being monitored to assess accuracy (recovery and precision). If direction cannot be obtained from the data user, the laboratory must spike at least one sample in duplicate per extraction batch of up to 20 samples with the analytes in Table 1. Spiked sample results should be reported only to the data user whose sample was spiked, or as requested or required by a regulatory/control authority, or in a permit.

8.3.1 If, as in compliance monitoring, the concentration of a specific analyte will be checked against a regulatory concentration limit, the concentration of the spike should be at that limit; otherwise, the concentration of the spike should be one to five times higher than the background concentration determined in section 8.3.2, at or near the mid-point of the calibration range, or at the concentration in the LCS (section 8.4) whichever concentration would be larger.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of the each analyte of interest. If necessary, prepare a new check sample concentrate (section 8.2.1) appropriate for the background concentration. Spike and analyze two additional sample aliquots, and determine the concentration after spiking (A_1 and A_2) of each analyte. Calculate the percent recoveries (P_1 and P_2) as $100(A_1 - B)/T$ and $100(A_2 - B)/T$, where T is the known true value of the spike. Also calculate the relative percent difference (RPD) between the concentrations (A_1 and A_2) as $200\sqrt{A_1 - A_2}/(A_1 + A_2)$. If necessary, adjust the concentrations used to calculate the RPD to account for differences in the volumes of the spiked aliquots.

8.3.3 Compare the percent recoveries (P_1 and P_2) and the RPD for each analyte in the MS/MSD aliquots with the corresponding QC acceptance criteria in Table 7. A laboratory may develop and apply QC acceptance

criteria more restrictive than the criteria in Table 7, if desired.

8.3.3.1 If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is suspect. See Section 8.1.7 for disposition of failures.

8.3.3.2 The acceptance criteria in Table 7 were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the spike to background ratio approaches 5:1 (Reference 13) and is applied to spike concentrations of 20 µg/L and higher. If spiking is performed at a concentration lower than 20 µg/L, the laboratory must use the QC acceptance criteria in Table 7, the optional QC acceptance criteria calculated for the specific spike concentration in Table 8, or optional in-house criteria (Section 8.3.4). To use the acceptance criteria in Table 8: (1) Calculate recovery (X') using the equation in Table 8, substituting the spike concentration (T) for C; (2) Calculate overall precision (S') using the equation in Table 8, substituting X' for \bar{X} ; (3) Calculate the range for recovery at the spike concentration as $(100 X'/T) \pm 2.44(100 S'/T)\%$ (Reference 4). For analytes of interest in Tables 1 and 2 not listed in Table 7, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 11 and 12). Alternatively, acceptance criteria may be based on laboratory control charts. In-house LCS QC acceptance criteria must be updated at least every two years.

8.3.4 After analysis of a minimum of 20 MS/MSD samples for each target analyte and surrogate, and if the laboratory chooses to develop and apply in-house QC limits, the laboratory should calculate and apply in-house QC limits for recovery and RPD of future MS/MSD samples (section 8.3). The QC limits for recovery are calculated as the mean observed recovery ± 3 standard deviations, and the upper QC limit for RPD is calculated as the mean RPD plus 3 standard deviations of the RPDs. The in-house QC limits must be updated at least every two years and re-established after any major change in the analytical instrumentation or process. If in-house QC limits are developed, at least 80% of the analytes tested in the MS/MSD must have in-house QC acceptance criteria that are tighter than those in Table 7 and the remaining analytes (those other than the analytes included in the 80%) must meet the acceptance criteria in Table 7. If an in-house QC limit for the RPD is greater than the limit in Table 7, then the limit in Table 7 must be used. Similarly, if an in-house lower limit for recovery is below the lower limit in Table 7, then the lower limit in Table 7 must be used, and if an in-house upper limit for recovery is above the upper limit in Table 7, then the upper limit in Table 7 must be used.

8.4 Calibration verification/laboratory control sample (LCS)—The working calibration curve or RF must be verified immediately after calibration and at the beginning of each 12-hour shift by the

measurement of an LCS. The LCS must be from a source different from the source used for calibration (section 7.3.2.1), but may be the same as the sample prepared for the DOC (section 8.2.1).

Note: The 12-hour shift begins after analysis of BFB, the LCS, and the blank, and ends 12 hours later. BFB, the LCS, and blank are outside of the 12-hour shift (Section 11.4). The MS and MSD are treated as samples and are analyzed within the 12-hour shift.

8.4.1 Prepare the LCS by adding QC check sample concentrate (section 8.2.1) to reagent water. Include all analytes of interest (Section 1.3) in the LCS. The volume of reagent water must be the same as the volume used for the sample, blank (Section 8.5), and MS/MSD (section 8.3). Also add an aliquot of the surrogate solution (Section 6.7) and internal standard solution (section 7.3.1.3). The concentration of the analytes in reagent water should be the same as the concentration in the DOC (section 8.2.2).

8.4.2 Analyze the LCS prior to analysis of field samples in the batch of samples analyzed during the 12-hour shift (see the **Note** at section 8.4). Determine the concentration (A) of each analyte. Calculate the percent recovery (Q) as $100(A/T)\%$, where T is the true value of the concentration in the LCS.

8.4.3 Compare the percent recovery (Q) for each analyte with its corresponding QC acceptance criterion in Table 7. For analytes of interest in Tables 1 and 2 not listed in Table 7, use the QC acceptance criteria developed for the LCS (section 8.4.5). If the recoveries for all analytes of interest fall within their respective QC acceptance criteria, analysis of blanks and field samples may proceed. If any individual Q falls outside the range, proceed according to section 8.4.4.

Note: The large number of analytes in Tables 1—2 present a substantial probability that one or more will fail the acceptance criteria when all analytes are tested simultaneously. Because a re-test is allowed in event of failure (sections 8.1.7 and 8.4.3), it may be prudent to analyze two LCSs together and evaluate results of the second analysis against the QC acceptance criteria only if an analyte fails the first test.

8.4.4 Repeat the test only for those analytes that failed to meet the acceptance criteria (Q). If these analytes now pass, system performance is acceptable and analysis of blanks and samples may proceed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, repeat the test (section 8.4.2), using a fresh LCS (section 8.2.2) or an LCS prepared with a fresh QC check sample concentrate (section 8.2.1), or perform and document system repair. Subsequent to repair, repeat the calibration verification/LCS test (section 8.4). If the acceptance criteria for Q cannot be met, re-calibrate the instrument (section 7). See section 8.1.7 for disposition of repeated failures.

Note: To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between the pair of tests.

8.4.5 After analysis of 20 LCS samples, and if the laboratory chooses to develop and apply in-house QC limits, the laboratory should calculate and apply in-house QC limits for recovery to future LCS samples (section 8.4). Limits for recovery in the LCS calculated as the mean recovery ± 3 standard deviations. A minimum of 80% of the analytes tested for in the LCS must have QC acceptance criteria tighter than those in Table 7, and the remaining analytes (those other than the analytes included in the 80%) must meet the acceptance criteria in Table 7. If an in-house lower limit for recovery is lower than the lower limit in Table 7, the lower limit in Table 7 must be used, and if an in-house upper limit for recovery is higher than the upper limit in Table 7, the upper limit in Table 7 must be used. Many of the analytes and surrogates do not have acceptance criteria. The laboratory should use 60–140% as interim acceptance criteria for recoveries of spiked analytes that do not have recovery limits specified in Table 7, and least 80% of the analytes should meet the 60–140% interim criteria until in-house LCS limits are developed. Alternatively, acceptance criteria for analytes that do not have recovery limits in Table 7 may be based on laboratory control charts. In-house QC acceptance criteria must be updated at least every two years.

8.5 Blank—A blank must be analyzed prior to each 12-hour shift to demonstrate freedom from contamination. A blank must also be analyzed after a sample containing a high concentration of an analyte or potentially interfering compound to demonstrate freedom from carry-over.

8.5.1 Spike the internal standards and surrogates into the blank. Analyze the blank immediately after analysis of the LCS (Section 8.4) and prior to analysis of the MS/MSD and samples to demonstrate freedom from contamination.

8.5.2 If any analyte of interest is found in the blank: At a concentration greater than the MDL for the analyte, at a concentration greater than one-third the regulatory compliance limit, or at a concentration greater than one-tenth the concentration in a sample analyzed during the 12-hour shift (section 8.4), *whichever is greater*; analysis of samples must be halted and samples affected by the blank must be re-analyzed. If, however, continued re-testing results in repeated blank contamination, the laboratory must document and report the failures (e.g., as qualifiers on results), unless the failures are not required to be reported as determined by the regulatory/control authority. Results associated with blank contamination for an analyte regulated in a discharge cannot be used to demonstrate regulatory compliance. QC failures do not relieve a discharger or permittee of reporting timely results.

8.6 Surrogate recoveries—The laboratory must evaluate surrogate recovery data in each sample against its in-house surrogate recovery limits for surrogates that do not have acceptance criteria in Table 7. The laboratory may use 60–140% as interim acceptance criteria for recoveries for surrogates not listed in Table 5. At least 80% of the surrogates must meet the 60–140% interim criteria until in-house limits are

developed. Alternatively, surrogate recovery limits may be developed from laboratory control charts.

8.6.1 Spike the surrogates into all samples, blanks, LCSs, and MS/MSDs. Compare surrogate recoveries against the QC acceptance criteria in Table 7. For surrogates in Table 5 without QC acceptance criteria in Table 7, and for other surrogates that may be used by the laboratory, limits must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 11 and 12). Alternatively, surrogate recovery limits may be developed from laboratory control charts. In-house QC acceptance criteria must be updated at least every two years.

8.6.2 If any recovery fails its criteria, attempt to find and correct the cause of the failure. See section 8.1.7 for disposition of failures.

8.7 Internal standard responses.

8.7.1 Calibration verification/LCS—The responses (GC peak heights or areas) of the internal standards in the calibration verification/LCS must be within 50% to 200% (1/2 to 2x) of their respective responses in the mid-point calibration standard. If they are not, repeat the LCS test using a fresh QC check sample (section 8.4.1) or perform and document system repair. Subsequent to repair, repeat the calibration verification/LCS test (section 8.4). If the responses are still not within 50% to 200%, re-calibrate the instrument (section 7) and repeat the calibration verification/LCS test.

8.7.2 Samples, blanks, and MS/MSDs—The responses (GC peak heights or areas) of each internal standard in each sample, blank, and MS/MSD must be within 50% to 200% (1/2 to 2x) of its respective response in the mid-point calibration standard. If, as a group, all internal standards are not within this range, perform and document system repair, repeat the calibration verification/LCS test (section 8.4), and re-analyze the affected samples. If a single internal standard is not within the 50% to 200% range, use an alternative internal standard for quantitation of the analyte referenced to the affected internal standard. It may be necessary to use the data system to calculate a new response factor from calibration data for the alternative internal standard/analyte pair. If an internal standard fails the 50–200% criteria and no analytes are detected in the sample, ignore the failure or report it if required by the regulatory/control authority.

8.8 As part of the QC program for the laboratory, control charts or statements of accuracy for wastewater samples must be assessed and records maintained periodically (see 40 CFR 136.7(c)(1)(viii)). After analysis of five or more spiked wastewater samples as in section 8.3, calculate the average percent recovery (P_x) and the standard deviation of the percent recovery (sp). Express the accuracy assessment as a percent interval from $P_x - 2_{sp}$ to $P_x + 2_{sp}$. For example, if $P_x = 90\%$ and $sp = 10\%$, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each analyte on a regular basis (e.g., after each 5–10 new accuracy measurements). If desired, statements of accuracy for laboratory performance, independent of performance on samples, may be developed using LCSs.

8.9 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Collect the sample as a grab sample in a glass container having a total volume of at least 25 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If needed, collect additional sample(s) for the MS/MSD (section 8.3).

9.2 Ice or refrigerate samples at $\leq 6^\circ\text{C}$ from the time of collection until analysis, but do not freeze. If residual chlorine is present, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottle just prior to shipping to the sampling site. Any method suitable for field use may be employed to test for residual chlorine (Reference 14). Field test kits are also available for this purpose. If sodium thiosulfate interferes in the determination of the analytes, an alternative preservative (e.g., ascorbic acid or sodium sulfite) may be used. If preservative has been added, shake the sample vigorously for one minute. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 If acrolein is to be determined, analyze the sample within 3 days. To extend the holding time to 14 days, acidify a separate sample to pH 4–5 with HCl using the procedure in section 9.7.

9.4 Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions (Reference 3). Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. To extend the holding time for aromatic compounds to 14 days, acidify the sample to approximately pH 2 using the procedure in section 9.7.

9.5 If halocarbons are to be determined, either use the acidified aromatics sample in section 9.4 or acidify a separate sample to a pH of about 2 using the procedure in section 9.7.

9.6 The ethers listed in Table 2 are prone to hydrolysis at pH 2 when a heated purge is used. Aqueous samples should not be acid preserved if these ethers are of interest, or if the alcohols they would form upon hydrolysis are of interest and the ethers are anticipated to present.

9.7 Sample acidification—Collect about 500 mL of sample in a clean container and adjust the pH of the sample to 4–5 for acrolein (section 9.3), or to about 2 for the aromatic compounds (section 9.4) by adding 1+1 HCl while swirling or stirring. Check the pH with narrow range pH paper. Fill a sample container as described in section 9.1. Alternatively, fill a precleaned vial (section

5.1.1) that contains approximately 0.25 mL of 1+1 HCl with sample as in section 9.1. If preserved using this alternative procedure, the pH of the sample can be verified to be <2 after some of the sample is removed for analysis. Acidification will destroy 2-chloroethylvinyl ether; therefore, determine 2-chloroethylvinyl ether from the unacidified sample.

9.8 All samples must be analyzed within 14 days of collection (Reference 3), unless specified otherwise in sections 9.3–9.7.

10. Sample Purging and Gas Chromatography

10.1 The footnote to Table 3 gives the suggested GC column and operating conditions MDLs and MLs for many of the analytes are given in Table 1. Retention times for many of the analytes are given in Table 3. Sections 10.2 through 10.7 suggest procedures that may be used with a manual purge-and-trap system. Auto-samplers and other columns or chromatographic conditions may be used if requirements in this method are met. Prior to performing analyses, and between analyses, it may be necessary to bake the purge-and-trap and GC systems (section 3.3).

10.2 Attach the trap inlet to the purging device, and set the purge-and-trap system to purge. Open the syringe valve located on the purging device sample introduction needle.

10.3 Allow the sample to come to ambient temperature prior to pouring an aliquot into the syringe. Remove the plunger from a syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add the surrogate spiking solution (section 6.7) and internal standard spiking solution (section 7.3.1.3) through the valve bore, then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. Autosamplers designed for purge-and-trap analysis of volatiles also may be used.

10.4 Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber.

10.5 Close both valves and purge the sample at a temperature, flow rate, and duration sufficient to purge the less-volatile analytes onto the trap, yet short enough to prevent blowing the more-volatile analytes through the trap. The temperature, flow rate, and time should be determined by test. The same purge temperature, flow rate, and purge time must be used for all calibration, QC, and field samples.

10.6 After the purge, set the purge-and-trap system to the desorb mode, and begin the temperature program of the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to the desorb temperature

while backflushing the trap with carrier gas at the flow rate and for the time necessary to desorb the analytes of interest. The optimum temperature, flow rate, and time should be determined by test. The same temperature, desorb time, and flow rate must be used for all calibration, QC, and field samples. If heating of the trap does not result in sharp peaks for the early eluting analytes, the GC column may be used as a secondary trap by cooling to an ambient or subambient temperature. To avoid carry-over and interferences, maintain the trap at the desorb temperature and flow rate until the analytes, interfering compounds, and excess water are desorbed. The optimum conditions should be determined by test.

10.7 Start MS data acquisition at the start of the desorb cycle and stop data collection when the analytes of interest, potentially interfering compounds, and water have eluted (see the footnote to Table 3 for conditions).

10.8 Cool the trap to the purge temperature and return the trap to the purge mode. When the trap is cool, the next sample can be analyzed.

11. Performance Tests

11.1 At the beginning of each 12-hour shift during which standards or samples will be analyzed, perform the tests in sections 11.2–11.3 to verify system performance. Use the instrument operating conditions in the footnotes to Table 3 for these performance tests. Alternative conditions may be used so as long as all QC requirements are met.

11.2 BFB—Inject 50 ng of BFB solution directly on the column. Alternatively, add BFB to reagent water or an aqueous standard such that 50 ng or less of BFB will be introduced into the GC. Analyze according to section 10. Confirm that all criteria in section 7.3.2.2 and Table 4 are met. If all criteria are not met, perform system repair, retune the mass spectrometer, and repeat the test until all criteria are met.

11.3 Verify calibration with the LCS (section 8.4) after the criteria for BFB are met (Reference 15) and prior to analysis of a blank or sample. After verification, analyze a blank (section 8.5) to demonstrate freedom from contamination and carry-over at the MDL. Tests for BFB, the LCS, and the blank are outside of the 12-hour shift, and the 12-hour shift includes samples and matrix spikes and matrix spike duplicates (section 8.4). The total time for analysis of BFB, the LCS, the blank, and the 12-hour shift must not exceed 14 hours.

12. Qualitative Identification

12.1 Identification is accomplished by comparison of results from analysis of a sample or blank with data stored in the GC/MS data system (section 7.3.2.3). Identification of an analyte is confirmed per sections 12.1.1 through 12.1.4.

12.1.1 The signals for the quantitation and secondary m/z's stored in the data system (section 7.3.2.3) for each analyte of interest must be present and must maximize within the same two consecutive scans.

12.1.2 The retention time for the analyte should be within ± 10 seconds of the analyte

in the LCS run at the beginning of the shift (section 8.4).

Note: Retention time windows other than ± 10 seconds may be appropriate depending on the performance of the gas chromatograph or observed retention time drifts due to certain types of matrix effects. Relative retention time (RRT) may be used as an alternative to absolute retention times if retention time drift is a concern. RRT is a unitless quantity (see section 20.2), although some procedures refer to “RRT units” in providing the specification for the agreement between the RRT values in the sample and the LCS or other standard. When significant retention time drifts are observed, dilutions or spiked samples may help the analyst determine the effects of the matrix on elution of the target analytes and to assist in qualitative identification.

12.1.3 Either the background corrected EICP areas, or the corrected relative intensities of the mass spectral peaks at the GC peak maximum, must agree within 50% to 200% ($\frac{1}{2}$ to 2 times) for the quantitation and secondary m/z's in the reference mass spectrum stored in the data system (section 7.3.2.3), or from a reference library. For example, if a peak has an intensity of 20% relative to the base peak, the analyte is identified if the intensity of the peak in the sample is in the range of 10% to 40% of the base peak.

12.1.4 If the acquired mass spectrum is contaminated, or if identification is ambiguous, an experienced spectrometrist (section 1.6) must determine the presence or absence of the compound.

12.2 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different gas chromatographic retention times. Sufficient gas chromatographic resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported.

13. Calculations

13.1 When an analyte has been identified, quantitation of that analyte is based on the integrated abundance from the EICP of the primary characteristic m/z in Table 5 or 6. Calculate the concentration using the response factor (RF) determined in section 7.3.3 and Equation 2. If a calibration curve was used, calculate the concentration using the regression equation for the curve. If the concentration of an analyte exceeds the calibration range, dilute the sample by the minimum amount to bring the concentration into the calibration range, and re-analyze. Determine a dilution factor (DF) from the amount of the dilution. For example, if the extract is diluted by a factor of 2, DF = 2.

$$C_s (\mu\text{g/L}) = \frac{A_s \times C_{is} \times DF}{A_{is} \times RF}$$

Equation 2

Where:

C_s = Concentration of the analyte in the sample, and the other terms are as defined in Section 7.3.3.

13.2 Reporting of results

As noted in section 1.4.1, EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described here are focused on such monitoring needs and may not be relevant to other uses of this method.

13.2.1 Report results for wastewater samples in $\mu\text{g/L}$ without correction for recovery. (Other units may be used if required by a permit.) Report all QC data with the sample results.

13.2.2 Reporting level. Unless otherwise specified in by a regulatory authority or in a discharge permit, results for analytes that meet the identification criteria are reported down to the concentration of the ML established by the laboratory through calibration of the instrument (see section 7.3.2 and the glossary for the derivation of the ML). EPA considers the terms "reporting limit," "limit of quantitation," "quantitation limit," and "minimum level" to be synonymous.

13.2.2.1 Report a result for each analyte in each field sample or QC standard at or above the ML to 3 significant figures. Report a result for each analyte found in each field sample or QC standard below the ML as "<ML," where ML is the concentration of the analyte at the ML, or as required by the regulatory/control authority or permit. Report a result for each analyte in a blank at or above the MDL to 2 significant figures. Report a result for each analyte found in a blank below the MDL as "<MDL," where MDL is the concentration of the analyte at the MDL, or as required by the regulatory/control authority or permit.

13.2.2.2 In addition to reporting results for samples and blanks separately, the concentration of each analyte in a blank associated with the sample may be subtracted from the result for that sample, but only if requested or required by a regulatory authority or in a permit. In this case, both the sample result and the blank result must be reported together.

13.2.2.3 Report a result for an analyte found in a sample that has been diluted at the least dilute level at which the area at the quantitation m/z is within the calibration range (*i.e.*, above the ML for the analyte) and the MS/MSD recovery and RPD are within their respective QC acceptance criteria (Table 7). This may require reporting results for some analytes from different analyses.

13.2.3 Results from tests performed with an analytical system that is not in control (*i.e.*, that does not meet acceptance criteria for any of the QC test in this method) must be documented and reported (*e.g.*, as a qualifier on results), unless the failure is not required to be reported as determined by the regulatory/control authority. Results

associated with a QC failure cannot be used to demonstrate regulatory compliance. QC failures do not relieve a discharger or permittee of reporting timely results. If the holding time would be exceeded for a re-analysis of the sample, the regulatory/control authority should be consulted for disposition.

14. Method Performance

14.1 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5–600 $\mu\text{g/L}$ (References 4 and 16). Single-operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 8.

14.2 As noted in section 1.1, this method was validated through an interlaboratory study conducted in the early 1980s. However, the fundamental chemistry principles used in this method remain sound and continue to apply.

15. Pollution Prevention

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operations. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, the laboratory should use pollution prevention techniques to address waste generation. When wastes cannot be reduced at the source, the Agency recommends recycling as the next best option.

15.2 The analytes in this method are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

15.3 For information about pollution prevention that may be applied to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW., Washington, DC 20036, 202-872-4477.

16. Waste Management

16.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. An overview of requirements can

be found in Environmental Management Guide for Small Laboratories (EPA 233-B-98-001).

16.2 Samples at $\text{pH} < 2$, or $\text{pH} > 12$, are hazardous and must be handled and disposed of as hazardous waste, or neutralized and disposed of in accordance with all federal, state, and local regulations. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, see "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Section 15.3.

16.3 Many analytes in this method decompose above 500 °C. Low-level waste such as absorbent paper, tissues, and plastic gloves may be burned in an appropriate incinerator. Gross quantities of neat or highly concentrated solutions of toxic or hazardous chemicals should be packaged securely and disposed of through commercial or governmental channels that are capable of handling these types of wastes.

16.4 For further information on waste management, consult "Waste Management Manual for Laboratory Personnel and Less is Better-Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW., Washington, DC 20036, 202-872-4477.

17. References

1. Bellar, T.A. and Lichtenberg, J.J. "Determining Volatile Organics at Microgram-per-Litre Levels by Gas Chromatography," Journal American Water Works Association, 66: 739 (1974).
2. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977.
3. Bellar, T.A. and Lichtenberg, J.J. "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," Measurement of Organic Pollutants in Water and Wastewater, C.E. Van Hall, editor, American Society for Testing and Materials, Philadelphia, PA. Special Technical Publication 686, 1978.
4. "EPA Method Study 29 EPA Method 624-Purgeables," EPA 600/4-84-054, National Technical Information Service, PB84-209915, Springfield, Virginia 22161, June 1984.
5. 40 CFR part 136, appendix B.

6. "Method Detection Limit for Methods 624 and 625," Olynyk, P., Budde, W.L., and Eichelberger, J.W. Unpublished report, May 14, 1980.

7. "Carcinogens-Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

8. "OSHA Safety and Health Standards, General Industry," (29 CFR part 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

9. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 7th Edition, 2003.

10. 40 CFR 136.6(b)(5)(x).

11. 40 CFR 136.6(b)(2)(i).

12. Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water (EPA-821-B-98-003) March 1999.

13. Provost, L.P. and Elder, R.S.

"Interpretation of Percent Recovery Data," American Laboratory, 15, 58-63 (1983).

14. 40 CFR 136.3(a), Table IB, Chlorine—Total residual.

15. Budde, W.L. and Eichelberger, J.W. "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-80-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, April 1980.

16. "Method Performance Data for Method 624," Memorandum from R. Slater and T. Pressley, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, January 17, 1984.

18. Tables

TABLE 1—PURGEABLES¹

Analyte	CAS Registry No.	MDL (µg/L) ²	ML (µg/L) ³
Acrolein	107-02-8
Acrylonitrile	107-13-1
Benzene	71-43-2	4.4	13.2
Bromodichloromethane	75-27-4	2.2	6.6
Bromoform	75-25-2	4.7	14.1
Bromomethane	74-83-9
Carbon tetrachloride	56-23-5	2.8	8.4
Chlorobenzene	108-90-7	6.0	18.0
Chloroethane	75-00-3
2-Chloroethylvinyl ether	110-75-8
Chloroform	67-66-3	1.6	4.8
Chloromethane	74-87-3
Dibromochloromethane	124-48-1	3.1	9.3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
1,1-Dichloroethane	75-34-3	4.7	14.1
1,2-Dichloroethane	107-06-2	2.8	8.4
1,1-Dichloroethene	75-35-4	2.8	8.4
trans-1,2-Dichloroethene	156-60-5	1.6	4.8
1,2-Dichloropropane	78-87-5	6.0	18.0
cis-1,3-Dichloropropene	10061-01-5	5.0	15.0
trans-1,3-Dichloropropene	10061-02-6
Ethyl benzene	100-41-4	7.2	21.6
Methylene chloride	75-09-2	2.8	8.4
1,1,2,2-Tetrachloroethane	79-34-5	6.9	20.7
Tetrachloroethene	127-18-4	4.1	12.3
Toluene	108-88-3	6.0	18.0
1,1,1-Trichloroethane	71-55-6	3.8	11.4
1,1,2-Trichloroethane	79-00-5	5.0	15.0
Trichloroethene	79-01-6	1.9	5.7
Vinyl chloride	75-01-4

¹ All the analytes in this table are Priority Pollutants (40 CFR part 423, appendix A).

² MDL values from the 1984 promulgated version of Method 624.

³ ML = Minimum Level—see Glossary for definition and derivation.

TABLE 2—ADDITIONAL PURGEABLES

Analyte	CAS Registry
Acetone ¹	67-64-1
Acetonitrile ²	75-05-8
Acrolein	107-02-8
Acrylonitrile	107-13-1
Allyl alcohol ¹	107-18-6
Allyl chloride	107-05-1
<i>t</i> -Amyl ethyl ether (TAE)	919-94-8
<i>t</i> -Amyl methyl ether (TAME)	994-058
Benzyl chloride	100-44-7
Bromoacetone ²	598-31-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
1,3-Butadiene	106-99-0
<i>n</i> -Butanol ¹	71-36-3

TABLE 2—ADDITIONAL PURGEABLES—Continued

Analyte	CAS Registry
2-Butanone (MEK) ^{1 2}	78-93-3
<i>t</i> -Butyl alcohol (TBA)	75-65-0
<i>n</i> -Butylbenzene	104-51-8
<i>sec</i> -Butylbenzene	135-98-8
<i>t</i> -Butylbenzene	98-06-6
<i>t</i> -Butyl ethyl ether (ETBE)	637-92-3
Carbon disulfide	75-15-0
Chloral hydrate ²	302-17-0
Chloroacetonitrile ¹	107-14-2
1-Chlorobutane	109-69-3
Chlorodifluoromethane	75-45-6
2-Chloroethanol ²	107-07-3
bis (2-Chloroethyl) sulfide ² ..	505-60-2

TABLE 2—ADDITIONAL PURGEABLES—Continued

Analyte	CAS Registry
1-Chlorohexanone	20261-68-1
Chloroprene (2-chloro-1,3-butadiene)	126-99-8
3-Chloropropene	107-05-1
3-Chloropropionitrile	542-76-7
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Crotonaldehyde ^{1 2}	123-73-9
Cyclohexanone	108-94-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
<i>cis</i> -1,4-Dichloro-2-butene	1476-11-5

TABLE 2—ADDITIONAL PURGEABLES—
Continued

Analyte	CAS Registry
<i>trans</i> -1,4-Dichloro-2-butene ..	110-57-6
<i>cis</i> -1,2-Dichloroethene	156-59-2
Dichlorodifluoromethane	75-71-8
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,3-Dichloro-2-propanol ²	96-23-1
1,1-Dichloropropene	563-58-6
<i>cis</i> -1,3-Dichloropropene	10061-01-5
1:2,3:4-Diepoxybutane	1464-53-5
Diethyl ether	60-29-7
Diisopropyl ether (DIPE)	108-20-3
1,4-Dioxane ²	123-91-1
Epichlorohydrin ²	106-89-8
Ethanol ²	64-17-5
Ethyl acetate ²	141-78-6
Ethyl methacrylate	97-63-2
Ethylene oxide ²	75-21-8
Hexachlorobutadiene	87-63-3
Hexachloroethane	67-72-1
2-Hexanone ²	591-78-6
Iodomethane	74-88-4
Isobutyl alcohol ¹	78-83-1
Isopropylbenzene	98-82-8
<i>p</i> -Isopropyltoluene	99-87-6
Methacrylonitrile ²	126-98-7
Methanol ²	67-56-1
Malonitrile ²	109-77-3
Methyl acetate	79-20-9
Methyl acrylate	96-33-3
Methyl cyclohexane	108-87-2
Methyl iodide	74-88-4
Methyl methacrylate	78-83-1
4-Methyl-2-pentanone (MIBK) ²	108-10-1
Methyl- <i>t</i> -butyl ether (MTBE)	1634-04-4
Naphthalene	91-20-3
Nitrobenzene	98-95-3
<i>N</i> -Nitroso- <i>di-n</i> -butylamine ² ..	924-16-3
2-Nitropropane	79-46-9
Paraldehyde ²	123-63-7
Pentachloroethane ²	76-01-7
Pentafluorobenzene	363-72-4
2-Pentanone ²	107-19-7
2-Picoline ²	109-06-8
1-Propanol ¹	71-23-8
2-Propanol ¹	67-63-0
Propargyl alcohol ²	107-19-7
<i>beta</i> -Propiolactone ²	57-58-8
Propionitrile (ethyl cyanide) ¹ ..	107-12-0
<i>n</i> -Propylamine	107-10-8
<i>n</i> -Propylbenzene	103-65-1
Pyridine ²	110-86-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
Tetrahydrofuran	109-99-9
<i>o</i> -Toluidine ²	95-53-4
1,2,3-Trichlorobenzene	87-61-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,3-Trimethylbenzene	526-73-8

TABLE 2—ADDITIONAL PURGEABLES—
Continued

Analyte	CAS Registry
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl acetate	108-05-4
<i>m</i> -Xylene ³	108-38-3
<i>o</i> -Xylene ³	95-47-6
<i>p</i> -Xylene ³	106-42-3
<i>m</i> + <i>o</i> -Xylene ³	179601-22-0
<i>m</i> + <i>p</i> -Xylene ³	179601-23-1
<i>o</i> + <i>p</i> -Xylene ³	136777-61-2

¹ Determined at a purge temperature of 80 °C.

² May be detectable at a purge temperature of 80 °C.

³ Determined in combination separated by GC column. Most GC columns will resolve *o*-xylene from *m*+*p*-xylene. Report using the CAS number for the individual xylene or the combination, as determined.

TABLE 3—EXAMPLE RETENTION TIMES

Analyte	Retention time (min)
Chloromethane	3.68
Vinyl chloride	3.92
Bromomethane	4.50
Chloroethane	4.65
Trichlorofluoromethane	5.25
Diethyl ether	5.88
Acrolein	6.12
1,1-Dichloroethene	6.30
Acetone	6.40
Iodomethane	6.58
Carbon disulfide	6.72
3-Chloropropene	6.98
Methylene chloride	7.22
Acrylonitrile	7.63
<i>trans</i> -1,2-Dichloroethene	7.73
1,1-Dichloroethane	8.45
Vinyl acetate	8.55
Allyl alcohol	8.58
2-Chloro-1,3-butadiene	8.65
Methyl ethyl ketone	9.50
<i>cis</i> -1,2-Dichloroethene	9.50
Ethyl cyanide	9.57
Methacrylonitrile	9.83
Chloroform	10.05
1,1,1-Trichloroethane	10.37
Carbon tetrachloride	10.70
Isobutanol	10.77
Benzene	10.98
1,2-Dichloroethane	11.00
Crotonaldehyde	11.45
Trichloroethene	12.08
1,2-Dichloropropane	12.37
Methyl methacrylate	12.55
<i>p</i> -Dioxane	12.63
Dibromomethane	12.65
Bromodichloromethane	12.95
Chloroacetonitrile	13.27

TABLE 3—EXAMPLE RETENTION
TIMES—Continued

Analyte	Retention time (min)
2-Chloroethylvinyl ether	13.45
<i>cis</i> -1,3-Dichloropropene	13.65
4-Methyl-2-pentanone	13.83
Toluene	14.18
<i>trans</i> -1,3-Dichloropropene	14.57
Ethyl methacrylate	14.70
1,1,2-Trichloroethane	14.93
1,3-Dichloropropane	15.18
Tetrachloroethene	15.22
2-Hexanone	15.30
Dibromochloromethane	15.68
1,2-Dibromoethane	15.90
Chlorobenzene	16.78
Ethylbenzene	16.82
1,1,1,2-Tetrachloroethane	16.87
<i>m</i> + <i>p</i> -Xylene	17.08
<i>o</i> -Xylene	17.82
Bromoform	18.27
Bromofluorobenzene	18.80
1,1,2,2-Tetrachloroethane	18.98
1,2,3-Trichloropropane	19.08
<i>trans</i> -1,4-Dichloro-2-butene ..	19.12

Column: 75 m x 0.53 mm ID x 3.0 µm wide-bore DB-624

Conditions: 40 °C for 4 min, 9 °C/min to 200 °C, 20 °C/min (or higher) to 250 °C, hold for 20 min at 250 °C to remove water.

Carrier gas flow rate: 6–7 mL/min at 40 °C.

Inlet split ratio: 3:1.

Interface split ratio: 7:2.

TABLE 4—BFB KEY *m/z* ABUNDANCE
CRITERIA¹

<i>m/z</i>	Abundance criteria
50	15–40% of <i>m/z</i> 95.
75	30–60% of <i>m/z</i> 95.
95	Base Peak, 100% Relative Abundance.
96	5–9% of <i>m/z</i> 95.
173	<2% of <i>m/z</i> 174.
174	>50% of <i>m/z</i> 95.
175	5–9% of <i>m/z</i> 174.
176	>95% but <101% of <i>m/z</i> 174.
177	5–9% of <i>m/z</i> 176.

¹ Abundance criteria are for a quadrupole mass spectrometer. Alternative tuning criteria from other published EPA reference methods may be used, provided method performance is not adversely affected. Alternative tuning criteria specified by an instrument manufacturer may also be used for another type of mass spectrometer, or for an alternative carrier gas, provided method performance is not adversely affected.

TABLE 5—SUGGESTED SURROGATE AND INTERNAL STANDARDS

Analyte	Retention time (min) ¹	Primary <i>m/z</i>	Secondary <i>m/z</i> 's
Benzene- <i>d</i> ₆	10.95	84
4-Bromofluorobenzene	18.80	95	174, 176
Bromochloromethane	9.88	128	49, 130, 51
2-Bromo-1-chloropropane	14.80	77	79, 156

TABLE 5—SUGGESTED SURROGATE AND INTERNAL STANDARDS—Continued

Analyte	Retention time (min) ¹	Primary m/z	Secondary m/z's
2-Butanone-d ₅	9.33	77
Chloroethane-d ₅	4.63	71
Chloroform- ¹³ C	10.00	86
1,2-Dichlorobenzene-d ₄	152
1,4-Dichlorobutane	18.57	55	90, 92
1,2-Dichloroethane-d ₄	10.88	102
1,1-Dichloroethene-d ₂	6.30	65
1,2-Dichloropropane-d ₆	12.27	67
<i>trans</i> -1,3-Dichloropropene-d ₄	14.50	79
1,4-Difluorobenzene	114	63, 88
Ethylbenzene-d ₁₀	16.77	98
Fluorobenzene	96	70
2-Hexanone-d ₅	15.30	63
Pentafluorobenzene	168
1,1,2,2-Tetrachloroethane-d ₂	18.93	84
Toluene-d ₈	14.13	100
Vinyl chloride-d ₃	3.87	65

¹ For chromatographic conditions, see the footnote to Table 3.

TABLE 6—CHARACTERISTIC m/z's FOR PURGEABLE ORGANICS

Analyte	Primary m/z	Secondary m/z's
Acrolein	56	55 and 58.
Acrylonitrile	53	52 and 51.
Chloromethane	50	52.
Bromomethane	94	96.
Vinyl chloride	62	64.
Chloroethane	64	66.
Methylene chloride	84	49, 51, and 86.
Trichlorofluoromethane	101	103.
1,1-Dichloroethene	96	61 and 98.
1,1-Dichloroethane	63	65, 83, 85, 98, and 100.
<i>trans</i> -1,2-Dichloroethene	96	61 and 98.
Chloroform	83	85.
1,2-Dichloroethane	98	62, 64, and 100.
1,1,1-Trichloroethane	97	99, 117, and 119.
Carbon tetrachloride	117	119 and 121.
Bromodichloromethane	83	127, 85, and 129.
1,2-Dichloropropane	63	112, 65, and 114.
<i>trans</i> -1,3-Dichloropropene	75	77.
Trichloroethene	130	95, 97, and 132.
Benzene	78
Dibromochloromethane	127	129, 208, and 206.
1,1,2-Trichloroethane	97	83, 85, 99, 132, and 134.
<i>cis</i> -1,3-Dichloropropene	75	77.
2-Chloroethylvinyl ether	106	63 and 65.
Bromoform	173	171, 175, 250, 252, 254, and 256.
1,1,2,2-Tetrachloroethane	168	83, 85, 131, 133, and 166.
Tetrachloroethene	164	129, 131, and 166.
Toluene	92	91.
Chlorobenzene	112	114.
Ethyl benzene	106	91.
1,3-Dichlorobenzene	146	148 and 111.
1,2-Dichlorobenzene	146	148 and 111.
1,4-Dichlorobenzene	146	148 and 111.

TABLE 7—LCS (Q), DOC (S AND \bar{X}), AND MS/MSD (P AND RPD) ACCEPTANCE CRITERIA ¹

Analyte	Range for Q (%)	Limit for s (%)	Range for \bar{X} (%)	Range for P ₁ , P ₂ (%)	Limit for RPD
Acrolein	60–140	30	50–150	40–160	60
Acrylonitrile	60–140	30	50–150	40–160	60
Benzene	65–135	33	75–125	37–151	61
Benzene-d ₆
Bromodichloromethane	65–135	34	50–140	35–155	56
Bromoform	70–130	25	57–156	45–169	42

TABLE 7—LCS (Q), DOC (S AND \bar{X}), AND MS/MSD (P AND RPD) ACCEPTANCE CRITERIA ¹—Continued

Analyte	Range for Q (%)	Limit for s (%)	Range for \bar{X} (%)	Range for P ₁ , P ₂ (%)	Limit for RPD
Bromomethane	15–185	90	D–206	D–242	61
2-Butanone-d ₅					
Carbon tetrachloride	70–130	26	65–125	70–140	41
Chlorobenzene	65–135	29	82–137	37–160	53
Chloroethane	40–160	47	42–202	14–230	78
Chloroethane-d ₅					
2-Chloroethylvinyl ether	D–225	130	D–252	D–305	71
Chloroform	70–135	32	68–121	51–138	54
Chloroform- ¹³ C					
Chloromethane	D–205	472	D–230	D–273	60
Dibromochloromethane	70–135	30	69–133	53–149	50
1,2-Dichlorobenzene	65–135	31	59–174	18–190	57
1,2-Dichlorobenzene-d ₄					
1,3-Dichlorobenzene	70–130	24	75–144	59–156	43
1,4-Dichlorobenzene	65–135	31	59–174	18–190	57
1,1-Dichloroethane	70–130	24	71–143	59–155	40
1,2-Dichloroethane	70–130	29	72–137	49–155	49
1,2-Dichloroethane-d ₄					
1,1-Dichloroethene	50–150	40	19–212	D–234	32
1,1-Dichloroethene-d ₂					
<i>trans</i> -1,2-Dichloroethene	70–130	27	68–143	54–156	45
1,2-Dichloropropane	35–165	69	19–181	D–210	55
1,2-Dichloropropane-d ₆					
<i>cis</i> -1,3-Dichloropropene	25–175	79	5–195	D–227	58
<i>trans</i> -1,3-Dichloropropene	50–150	52	38–162	17–183	86
<i>trans</i> -1,3-Dichloropropene-d ₄					
Ethyl benzene	60–140	34	75–134	37–162	63
2-Hexanone-d ₅					
Methylene chloride	60–140	192	D–205	D–221	28
1,1,2,2-Tetrachloroethane	60–140	36	68–136	46–157	61
1,1,2,2-Tetrachloroethane-d ₂					
Tetrachloroethene	70–130	23	65–133	64–148	39
Toluene	70–130	22	75–134	47–150	41
Toluene-d ₈					
1,1,1-Trichloroethane	70–130	21	69–151	52–162	36
1,1,2-Trichloroethane	70–130	27	75–136	52–150	45
Trichloroethene	65–135	29	75–138	70–157	48
Trichlorofluoromethane	50–150	50	45–158	17–181	84
Vinyl chloride	5–195	100	D–218	D–251	66
Vinyl chloride-d ₃					

¹ Criteria were calculated using an LCS concentration of 20 µg/L.

Q = Percent recovery in calibration verification/LCS (section 8.4).

s = Standard deviation of percent recovery for four recovery measurements (section 8.2.4).

\bar{X} = Average percent recovery for four recovery measurements (section 8.2.4).

P = Percent recovery for the MS or MSD (section 8.3.3).

D = Detected; result must be greater than zero.

Notes:

1. Criteria for pollutants are based upon the method performance data in Reference 4. Where necessary, limits have been broadened to assure applicability to concentrations below those used to develop Table 7.

2. Criteria for surrogates are from EPA CLP SOM01.2D.

TABLE 8—RECOVERY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Analyte	Recovery, X' (µg/L)	Single analyst precision, s' (µg/L)	Overall precision, S' (µg/L)
Benzene	0.93C+2.00	20.26 \bar{X} – 1.74	0.25 \bar{X} – 1.33
Bromodichloromethane	1.03C – 1.58	0.15 \bar{X} +0.59	0.20 \bar{X} +1.13
Bromoform	1.18C – 2.35	0.12 \bar{X} +0.36	0.17 \bar{X} +1.38
Bromomethane ^a	1.00C	0.43 \bar{X}	0.58 \bar{X}
Carbon tetrachloride	1.10C – 1.68	0.12 \bar{X} +0.25	0.11 \bar{X} +0.37
Chlorobenzene	0.98C+2.28	0.16 \bar{X} – 0.09	0.26 \bar{X} – 1.92
Chloroethane	1.18C+0.81	0.14 \bar{X} +2.78	0.29 \bar{X} +1.75
2-Chloroethylvinyl ether ^a	1.00C	0.62 \bar{X}	0.84 \bar{X}
Chloroform	0.93C+0.33	0.16 \bar{X} +0.22	0.18 \bar{X} +0.16
Chloromethane	1.03C+0.81	0.37 \bar{X} +2.14	0.58 \bar{X} +0.43
Dibromochloromethane	1.01C – 0.03	0.17 \bar{X} – 0.18	0.17 \bar{X} +0.49
1,2-Dichlorobenzene ^b	0.94C+4.47	0.22 \bar{X} – 1.45	0.30 \bar{X} – 1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14 \bar{X} – 0.48	0.18 \bar{X} – 0.82

TABLE 8—RECOVERY AND PRECISION AS FUNCTIONS OF CONCENTRATION—Continued

Analyte	Recovery, \bar{X} ($\mu\text{g/L}$)	Single analyst precision, s_r ($\mu\text{g/L}$)	Overall precision, S_r ($\mu\text{g/L}$)
1,4-Dichlorobenzene ^b	0.94C+4.47	0.22 \bar{X} – 1.45	0.30 \bar{X} – 1.20
1,1-Dichloroethane	1.05C+0.36	0.13 \bar{X} – 0.05	0.16 \bar{X} + 0.47
1,2-Dichloroethane	1.02C+0.45	0.17 \bar{X} – 0.32	0.21 \bar{X} – 0.38
1,1-Dichloroethene	1.12C+0.61	0.17 \bar{X} + 1.06	0.43 \bar{X} – 0.22
<i>trans</i> -1,2-Dichloroethene	1.05C+0.03	0.14 \bar{X} – +0.09	0.19 \bar{X} – +0.17
1,2-Dichloropropane ^a	1.00C	0.33 \bar{X}	0.45 \bar{X}
<i>cis</i> -1,3-Dichloropropene ^a	1.00C	0.38 \bar{X}	0.52 \bar{X}
<i>trans</i> -1,3-Dichloropropene ^a	1.00C	0.25 \bar{X}	0.34 \bar{X}
Ethyl benzene	0.98C+2.48	0.14 \bar{X} + 1.00	0.26 \bar{X} – 1.72
Methylene chloride	0.87C+1.88	0.15 \bar{X} + 1.07	0.32 \bar{X} + 4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16 \bar{X} + 0.69	0.20 \bar{X} + 0.41
Tetrachloroethene	1.06C+0.60	0.13 \bar{X} – 0.18	0.16 \bar{X} – 0.45
Toluene	0.98C+2.03	0.15 \bar{X} – 0.71	0.22 \bar{X} – 1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12 \bar{X} – 0.15	0.21 \bar{X} – 0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14 \bar{X} + 0.02	0.18 \bar{X} + 0.00
Trichloroethene	1.04C+2.27	0.13 \bar{X} + 0.36	0.12 \bar{X} + 0.59
Trichlorofluoromethane	0.99C+0.39	0.33 \bar{X} – 1.48	0.34 \bar{X} – 0.39
Vinyl chloride	1.00C	0.48 \bar{X}	0.65 \bar{X}

\bar{X} = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$.

S_r = Expected single analyst standard deviation of measurements at an average concentration found of \bar{X} , in $\mu\text{g/L}$.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of \bar{X} , in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

\bar{X} = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.

^a Estimates based upon the performance in a single laboratory (References 4 and 16).

^b Due to coelutions, performance statements for these isomers are based upon the sums of their concentrations.

19. Glossary

These definitions and purposes are specific to this method, but have been conformed to common usage to the extent possible.

19.1 Units of weight and measure and their abbreviations.

19.1.1 Symbols.

°C degrees Celsius

μg microgram

μL microliter

< less than

> greater than

% percent

19.1.2 Abbreviations (in alphabetical order).

cm centimeter

g gram

h hour

ID inside diameter

in. inch

L liter

m mass

mg milligram

min minute

mL milliliter

mm millimeter

ms millisecond

m/z mass-to-charge ratio

N normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution

ng nanogram

pg picogram

ppb part-per-billion

ppm part-per-million

ppt part-per-trillion

psig pounds-per-square inch gauge

v/v volume per unit volume

w/v weight per unit volume

19.2 Definitions and acronyms (in alphabetical order).

Analyte—A compound tested for by this method. The analytes are listed in Tables 1 and 2.

Analyte of interest—An analyte of interest is an analyte required to be determined by a regulatory/control authority or in a permit, or by a client.

Analytical batch—The set of samples analyzed on a given instrument during a 12-hour period that begins with analysis of a calibration verification/LCS. See section 8.4.

Blank—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus. See section 8.5.

Calibration—The process of determining the relationship between the output or response of a measuring instrument and the value of an input standard. Historically, EPA has referred to a multi-point calibration as the “initial calibration,” to differentiate it from a single-point calibration verification.

Calibration standard—A solution prepared from stock solutions and/or a secondary standards and containing the analytes of interest, surrogates, and internal standards. The calibration standard is used to calibrate the response of the GC/MS instrument against analyte concentration.

Calibration verification standard—The laboratory control sample (LCS) used to verify calibration. See Section 8.4.

Descriptor—In SIM, the beginning and ending retention times for the RT window, the m/z's sampled in the RT window, and the dwell time at each m/z.

Extracted ion current profile (EICP)—The line described by the signal at a given m/z.

Field duplicates—Two samples collected at the same time and place under identical conditions, and treated identically throughout field and laboratory procedures. Results of analyses of field duplicates provide an estimate of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Field blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC—Gas chromatograph or gas chromatography.

Internal standard—A compound added to a sample in a known amount and used as a reference for quantitation of the analytes of interest and surrogates. Internal standards are listed in Table 5. Also see Internal standard quantitation.

Internal standard quantitation—A means of determining the concentration of an analyte of interest (Tables 1 and 2) by reference to a compound added to a sample and not expected to be found in the sample.

DOC—Initial demonstration of capability (DOC; section 8.2); four aliquots of reagent water spiked with the analytes of interest and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. A DOC is performed prior to the first time this method is used and any time the method or instrumentation is modified.

Laboratory control sample (LCS; laboratory fortified blank (LFB); on-going precision and

recovery sample; OPR)—An aliquot of reagent water spiked with known quantities of the analytes of interest and surrogates. The LCS is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery. In this method, the LCS is synonymous with a calibration verification sample (See sections 7.4 and 8.4).

Laboratory fortified sample matrix—See Matrix spike.

Laboratory reagent blank—See Blank.

Matrix spike (MS) and matrix spike duplicate (MSD) (laboratory fortified sample matrix and duplicate)—Two aliquots of an environmental sample to which known quantities of the analytes of interest and surrogates are added in the laboratory. The MS/MSD are prepared and analyzed exactly like a field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

May—This action, activity, or procedural step is neither required nor prohibited.

May not—This action, activity, or procedural step is prohibited.

Method blank (laboratory reagent blank)—See Blank.

Method detection limit (MDL)—A detection limit determined by the procedure at 40 CFR part 136, appendix B. The MDLs determined by EPA in the original version of the method are listed in Table 1. As noted in Sec. 1.4, use the MDLs in Table 1 in conjunction with current MDL data from the laboratory actually analyzing samples to assess the sensitivity of this procedure relative to project objectives and regulatory requirements (where applicable).

Minimum level (ML)—The term “minimum level” refers to either the sample concentration equivalent to the lowest calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher. Minimum levels may be obtained in several ways: They may be published in a method; they may be based on the lowest acceptable calibration point used by a laboratory; or they may be calculated by multiplying the MDL in a method, or the MDL determined by a laboratory, by a factor of 3. For the purposes of NPDES compliance monitoring, EPA considers the following terms to be synonymous: “quantitation limit,” “reporting limit,” and “minimum level.”

MS—Mass spectrometer or mass spectrometry.

Must—This action, activity, or procedural step is required.

m/z—The ratio of the mass of an ion (m) detected in the mass spectrometer to the charge (z) of that ion.

Quality control sample (QCS)—A sample containing analytes of interest at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards.

The purpose is to check laboratory performance using test materials that have been prepared independent of the normal preparation process.

Reagent water—Water demonstrated to be free from the analytes of interest and potentially interfering substances at the MDLs for the analytes in this method.

Regulatory compliance limit (or regulatory concentration limit)—A limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory/control authority.

Relative retention time (RRT)—The ratio of the retention time of an analyte to the retention time of its associated internal standard. RRT compensates for small changes in the GC temperature program that can affect the absolute retention times of the analyte and internal standard. RRT is a unitless quantity.

Relative standard deviation (RSD)—The standard deviation times 100 divided by the mean. Also termed “coefficient of variation.”

RF—Response factor. See section 7.3.3.

RSD—See relative standard deviation.

Safety Data Sheet (SDS)—Written information on a chemical's toxicity, health hazards, physical properties, fire, and reactivity, including storage, spill, and handling precautions that meet the requirements of OSHA, 29 CFR 1910.1200(g) and appendix D to § 1910.1200. United Nations Globally Harmonized System of Classification and Labelling of Chemicals (GHS), third revised edition, United Nations, 2009.

Selected Ion Monitoring (SIM)—An MS technique in which a few m/z's are monitored. When used with gas chromatography, the m/z's monitored are usually changed periodically throughout the chromatographic run to correlate with the characteristic m/z's for the analytes, surrogates, and internal standards as they elute from the chromatographic column. The technique is often used to increase sensitivity and minimize interferences.

Signal-to-noise ratio (S/N)—The height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the width of the noise.

SIM—See Selection Ion Monitoring.

Should—This action, activity, or procedural step is suggested but not required.

Stock solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

Surrogate—A compound unlikely to be found in a sample, and which is spiked into sample in a known amount before purge-and-trap. The surrogate is quantitated with the same procedures used to quantitate the analytes of interest. The purpose of the surrogate is to monitor method performance with each sample.

VOA—Volatile organic analysis: e.g., the analysis performed by this method.

Method 625.1—Base/Neutrals and Acids by GC/MS

1. Scope and Application

1.1 This method is for determination of semivolatile organic pollutants in industrial discharges and other environmental samples by gas chromatography combined with mass spectrometry (GC/MS), as provided under 40 CFR 136.1. This revision is based on a previous protocol (Reference 1), on the basic revision promulgated October 26, 1984, and on an interlaboratory method validation study (Reference 2). Although this method was validated through an interlaboratory study conducted in the early 1980s, the fundamental chemistry principles used in this method remain sound and continue to apply.

1.2 The analytes that may be qualitatively and quantitatively determined using this method and their CAS Registry numbers are listed in Tables 1 and 2. The method may be extended to determine the analytes listed in Table 3; however, extraction or gas chromatography of some of these analytes may make quantitative determination difficult. For example, benzidine is subject to oxidative losses during extraction and/or solvent concentration. Under the alkaline conditions of the extraction, *alpha*-BHC, *gamma*-BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodiphenylamine and other nitrosoamines may decompose in the gas chromatographic inlet. The sample may be extracted at neutral pH if necessary to overcome these or other decomposition problems that could occur at alkaline or acidic pH. EPA also has provided other methods (e.g., Method 607—Nitrosamines) that may be used for determination of some of these analytes. EPA encourages use of Method 625.1 to determine additional compounds amenable to extraction and GC/MS.

1.3 The large number of analytes in Tables 1–3 of this method makes testing difficult if all analytes are determined simultaneously. Therefore, it is necessary to determine and perform quality control (QC) tests for the “analytes of interest” only. Analytes of interest are those required to be determined by a regulatory/control authority or in a permit, or by a client. If a list of analytes is not specified, the analytes in Tables 1 and 2 must be determined, at a minimum, and QC testing must be performed for these analytes. The analytes in Tables 1 and 2, and some of the analytes in Table 3 have been identified as Toxic Pollutants (40 CFR 401.15), expanded to a list of Priority Pollutants (40 CFR part 423, appendix A).

1.4 In this revision to Method 625, the pesticides and polychlorinated biphenyls (PCBs) have been moved from Table 1 to Table 3 (Additional Analytes) to distinguish these analytes from the analytes required in quality control tests (Tables 1 and 2). QC acceptance criteria for pesticides and PCBs have been retained in Table 6 and may continue to be applied if desired, or if requested or required by a regulatory/control

authority or in a permit. Method 608.3 should be used for determination of pesticides and PCBs. However, if pesticides and/or PCBs are to be determined, an additional sample must be collected and extracted using the pH adjustment and extraction procedures specified in Method 608.3. Method 1668C may be useful for determination of PCBs as individual chlorinated biphenyl congeners, and Method 1699 may be useful for determination of pesticides. At the time of writing of this revision, Methods 1668C and 1699 had not been approved for use at 40 CFR part 136. The screening procedure for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) contained in the version of Method 625 promulgated October 26, 1984 has been replaced with procedures for selected ion monitoring (SIM), and 2,3,7,8-TCDD may be determined using the SIM procedures. However, EPA Method 613 or 1613B should be used for analyte-specific determination of 2,3,7,8-TCDD because of the focus of these methods on this compound. Methods 613 and 1613B are approved for use at 40 CFR part 136.

1.5 Method detection limits (MDLs; Reference 3) for the analytes in Tables 1, 2, and 3 are listed in those tables. These MDLs were determined in reagent water (Reference 4). Advances in analytical technology, particularly the use of capillary (open-tubular) columns, allowed laboratories to routinely achieve MDLs for the analytes in this method that are 2–10 times lower than those in the version promulgated in 1984. The MDL for an analyte in a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5.1 EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described in section 15.2 are focused on such monitoring needs and may not be relevant to other uses of the method.

1.5.2 This method includes “reporting limits” based on EPA’s “minimum level” (ML) concept (see the glossary in section 22). Tables 1, 2, and 3 contain MDL values and ML values for many of the analytes.

1.6 This method is performance-based. It may be modified to improve performance (e.g., to overcome interferences or improve the accuracy of results) provided all performance requirements are met.

1.6.1 Examples of allowed method modifications are described at 40 CFR 136.6. Other examples of allowed modifications specific to this method, including solid-phase extraction (SPE) are described in section 8.1.2.

1.6.2 Any modification beyond those expressly permitted at 40 CFR 136.6 or in section 8.1.2 of this method shall be considered a major modification subject to application and approval of an alternate test procedure under 40 CFR 136.4 and 136.5.

1.6.3 For regulatory compliance, any modification must be demonstrated to produce results equivalent or superior to results produced by this method when applied to relevant wastewaters (section 8.3).

1.7 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 8.2.

1.8 Terms and units of measure used in this method are given in the glossary at the end of the method.

2. Summary of Method

2.1 A measured volume of sample, sufficient to meet an MDL or reporting limit, is serially extracted with methylene chloride at pH 11–13 and again at a pH less than 2 using a separatory funnel or continuous liquid/liquid extractor.

2.2 The extract is concentrated to a volume necessary to meet the required compliance or detection limit, and analyzed by GC/MS. Qualitative identification of an analyte in the extract is performed using the retention time and the relative abundance of two or more characteristic masses (*m/z*’s). Quantitative analysis is performed using the internal standard technique with a single characteristic *m/z*.

3. Contamination and Interferences

3.1 Solvents, reagents, glassware, and other sample processing labware may yield artifacts, elevated baselines, or matrix interferences causing misinterpretation of chromatograms and mass spectra. All materials used in the analysis must be demonstrated to be free from contamination and interferences by analyzing blanks initially and with each extraction batch (samples started through the extraction process in a given 24-hour period, to a maximum of 20 samples—see Glossary for detailed definition), as described in Section 8.5. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, labware is cleaned by extraction or solvent rinse, or baking in a kiln or oven.

3.2 Glassware must be scrupulously cleaned (Reference 5). Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and reagent water. The glassware should then be drained dry, and heated at 400 °C for 15–30 minutes. Some thermally stable materials, such as PCBs, may require higher temperatures and longer baking times for removal. Solvent rinses with pesticide quality acetone, hexane, or other solvents may be substituted for heating. Do not heat volumetric labware above 90 °C. After drying and cooling, store inverted or capped with solvent-rinsed or baked aluminum foil in a clean environment to prevent accumulation of dust or other contaminants.

3.3 Matrix interferences may be caused by contaminants co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. Interferences extracted from samples high in total organic carbon (TOC) may result in elevated baselines, or by

enhancing or suppressing a signal at or near the retention time of an analyte of interest. Analyses of the matrix spike and duplicate (section 8.3) may be useful in identifying matrix interferences, and gel permeation chromatography (GPC; Section 11.1) and sulfur removal (section 11.2) may aid in eliminating these interferences. EPA has provided guidance that may aid in overcoming matrix interferences (Reference 6).

3.4 In samples that contain an inordinate number of interferences, the use of chemical ionization (CI) or triple quadrupole (MRM) mass spectrometry may make identification easier. Tables 4 and 5 give characteristic CI and MRM *m/z*’s for many of the analytes covered by this method. The use of CI or MRM mass spectrometry may be utilized to support electron ionization (EI) mass spectrometry or as a primary method for identification and quantification. While the use of these enhanced techniques is encouraged, it is not required.

4. Safety

4.1 Hazards associated with each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDSs, OSHA, 29 CFR 1910.1200(g)) should also be made available to all personnel involved in sample handling and chemical analysis. Additional references to laboratory safety are available and have been identified (References 7–9) for the information of the analyst.

4.2 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: Benzo(a)anthracene, benzidine, 3,3’-dichlorobenzidine, benzo(a)pyrene, *alpha*-BHC, *beta*-BHC, *delta*-BHC, *gamma*-BHC, Dibenz(a,h)-anthracene, N-nitrosodimethylamine, 4,4’-DDT, and PCBs. Other compounds in Table 3 may also be toxic. Primary standards of toxic compounds should be prepared in a chemical fume hood, and a NIOSH/MESA approved toxic gas respirator should be worn when handling high concentrations of these compounds.

4.3 This method allows the use of hydrogen as a carrier gas in place of helium (section 5.6.1.2). The laboratory should take the necessary precautions in dealing with hydrogen, and should limit hydrogen flow at the source to prevent buildup of an explosive mixture of hydrogen in air.

5. Apparatus and Materials

Note: Brand names, suppliers, and part numbers are for illustration purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here. Demonstrating that the equipment and supplies used in the laboratory achieves the required performance is the responsibility of the laboratory.

Suppliers for equipment and materials in this method may be found through an on-line search. Please do not contact EPA for supplier information.

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—amber glass bottle large enough to contain the necessary sample volume, fitted with a fluoropolymer-lined screw cap. Foil may be substituted for fluoropolymer if the sample is not corrosive. If amber bottles are not available, protect samples from light. Unless pre-cleaned, the bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—the sampler must incorporate a pre-cleaned glass sample container. Samples must be kept refrigerated at $\leq 6^{\circ}\text{C}$ and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, rinse the compressible tubing with methanol, followed by repeated rinsing with reagent water, to minimize the potential for sample contamination. An integrating flow meter is required to collect flow-proportioned composites.

5.2 Glassware.

5.2.1 Separatory funnel—Size appropriate to hold sample volume and extraction solvent volume, and equipped with fluoropolymer stopcock.

5.2.2 Drying column—Chromatographic column, approximately 400 mm long by 19 mm ID, with coarse frit, or equivalent, sufficient to hold 15 g of anhydrous sodium sulfate.

5.2.3 Concentrator tube, Kuderna-Danish—10 mL, graduated (Kontes 570050–1025 or equivalent). Calibration must be checked at the volumes employed in the test. A ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500 mL (Kontes 57001–0500 or equivalent). Attach to concentrator tube with springs.

Note: Use of a solvent recovery system with the K–D or other solvent evaporation apparatus is strongly recommended.

5.2.5 Snyder column, Kuderna-Danish—Three-ball macro (Kontes 503000–0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball micro (Kontes 569001–0219 or equivalent).

5.2.7 Vials—10–15 mL, amber glass, with Teflon-lined screw cap.

5.2.8 Continuous liquid-liquid extractor—Equipped with fluoropolymer or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, NJ, P/N 6848–20, or equivalent.)

5.2.9 In addition to the glassware listed above, the laboratory should be equipped with all necessary pipets, volumetric flasks, beakers, and other glassware listed in this method and necessary to perform analyses successfully.

5.3 Boiling chips—Approximately 10/40 mesh, glass, silicon carbide, or equivalent. Heat to 400°C for 30 minutes, or solvent

rinse or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control ($\pm 2^{\circ}\text{C}$). The bath should be used in a hood.

5.5 Balances.

5.5.1 Analytical, capable of accurately weighing 0.1 mg.

5.5.2 Top loading, capable of accurately weighing 10 mg.

5.6 GC/MS system.

5.6.1 Gas chromatograph (GC)—An analytical system complete with a temperature programmable gas chromatograph and all required accessories, including syringes and analytical columns.

5.6.1.1 Injection port—Can be split, splitless, temperature programmable vaporization split/splitless (PTV), solvent-purge, large-volume, on-column, backflushed, or other. An autosampler is highly recommended because it injects volumes more precisely than volumes injected manually.

5.6.1.2 Carrier gas—Helium or hydrogen. Data in the tables in this method were obtained using helium carrier gas. If hydrogen is used, analytical conditions may need to be adjusted for optimum performance, and calibration and all QC tests must be performed with hydrogen carrier gas. See Section 4.3 for precautions regarding the use of hydrogen as a carrier gas.

5.6.2 GC column—See the footnotes to Tables 4 and 5. Other columns or column systems may be used provided all requirements in this method are met.

5.6.3 Mass spectrometer—Capable of repetitively scanning from 35–450 Daltons (amu) every two seconds or less, utilizing a 70 eV (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9A or 9B when 50 ng or less of decafluorotriphenyl phosphine (DFTPP; CAS 5074–71–5; bis(pentafluorophenyl) phenyl phosphine) is injected into the GC.

5.6.4 GC/MS interface—Any GC to MS interface that meets all performance requirements in this method may be used.

5.6.5 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage of mass spectra acquired throughout the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z 's (masses) and plotting m/z abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP).

Software must also be available that allows integrating the abundance at any EICP between specified time or scan number limits.

5.7 Automated gel permeation chromatograph (GPC).

5.7.1 GPC column—150–700 mm long \times 21–25 mm ID, packed with 70 g of SX–3 Bio beads; Bio-Rad Labs, or equivalent.

5.7.2 Pump, injection valve, UV detector, and other apparatus necessary to meet the requirements in this method.

5.8 Nitrogen evaporation device—Equipped with a water bath than can be maintained at $30\text{--}45^{\circ}\text{C}$; N-Evap, Organomation Associates, or equivalent.

5.9 Muffle furnace or kiln—Capable of baking glassware or sodium sulfate in the range of $400\text{--}450^{\circ}\text{C}$.

6. Reagents

6.1 Reagent water—Reagent water is defined as water in which the analytes of interest and interfering compounds are not detected at the MDLs of the analytes of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) granular.

6.4 Sulfuric acid (1+1)—Slowly add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, methylene chloride, 2-propanol—High purity pesticide quality, or equivalent, demonstrated to be free of the analytes of interest and interferences (Section 3). Purification of solvents by distillation in all-glass systems may be required.

6.6 Sodium sulfate—(ACS) granular, anhydrous, rinsed or Soxhlet extracted with methylene chloride (20 mL/g), baked in a shallow tray at 450°C for one hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw cap that prevents moisture from entering.

6.7 Stock standard solutions (1.00 $\mu\text{g}/\mu\text{L}$)—Stock standard solutions may be prepared from pure materials, or purchased as certified solutions. Traceability must be to the National Institute of Standards and Technology (NIST) or other national or international standard, when available. Stock solution concentrations alternate to those below may be used. Because of the toxicity of some of the compounds, primary dilutions should be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations of neat materials are handled. The following procedure may be used to prepare standards from neat materials.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality methanol or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the convenience of the laboratory. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Unless stated otherwise in this method, store non-aqueous standards in fluoropolymer-lined screw-cap, or heat-sealed, glass containers, in the dark at -20 to -10°C . Store aqueous standards; e.g., the aqueous LCS (section 8.4.1), in the dark at $\leq 6^{\circ}\text{C}$, but do not freeze. Standards prepared by the laboratory may be stored for up to one year, except when comparison with QC check standards indicates that a standard has degraded or become more concentrated due to evaporation, or unless the laboratory has data on file to prove stability for a longer period. Commercially prepared standards may be stored until the expiration date provided by the vendor, except when

comparison with QC check standards indicates that a standard has degraded or become more concentrated due to evaporation, or unless the laboratory has data from the vendor on file to prove stability for a longer period.

6.8 Surrogate standard spiking solution.

6.8.1 Select a minimum of three surrogate compounds from Table 8 that most closely match the recovery of the analytes of interest. For example, if all analytes tested are considered acids, use surrogates that have similar chemical attributes. Other compounds may be used as surrogates so long as they do not interfere in the analysis. If only one or two analytes are determined, one or two surrogates may be used.

6.8.2 Prepare a solution containing each selected surrogate such that the concentration in the sample would match the concentration in the mid-point calibration standard. For example, if the midpoint of the calibration is 100 µg/L, prepare the spiking solution at a concentration of 100 µg/mL in methanol. Addition of 1.00 mL of this solution to 1000 mL of sample will produce a concentration of 100 µg/L of the surrogate. Alternate volumes and concentrations appropriate to the response of the GC/MS instrument or for selective ion monitoring (SIM) may be used, if desired. Store per section 6.7.2.

6.9 Internal standard spiking solution.

6.9.1 Select three or more internal standards similar in chromatographic behavior to the analytes of interest. Internal standards are listed in Table 8. Suggested internal standards are: 1,4-dichlorobenzene-*d*₄; naphthalene-*d*₈; acenaphthene-*d*₁₀; phenanthrene-*d*₁₀; chrysene-*d*₁₂; and perylene-*d*₁₂. The laboratory must demonstrate that measurement of the internal standards is not affected by method or matrix interferences (see also section 7.3.4).

6.9.2 Prepare the internal standards at a concentration of 10 mg/mL in methylene chloride or other suitable solvent. When 10 µL of this solution is spiked into a 1-mL extract, the concentration of the internal standards will be 100 µg/mL. A lower concentration appropriate to the response of the GC/MS instrument or for SIM may be used, if desired. Store per section 6.7.3.

6.9.3 To assure accurate analyte identification, particularly when SIM is used, it may be advantageous to include more internal standards than those suggested in section 6.9.1. An analyte will be located most accurately if its retention time relative to an internal standard is in the range of 0.8 to 1.2.

6.10 DFTPP standard—Prepare a solution of DFTPP in methanol or other suitable solvent such that 50 ng or less will be injected (see section 13.2). An alternative concentration may be used to compensate for specific injection volumes or to assure that the operating range of the instrument is not exceeded, so long as the total injected is 50 ng or less. Include benzidine and pentachlorophenol in this solution such that ≤100 ng of benzidine and ≤50 ng of pentachlorophenol will be injected.

6.11 Quality control check sample concentrate—See section 8.2.1.

6.12 GPC calibration solution.

6.12.1 Prepare a methylene chloride solution to contain corn oil, bis(2-ethylhexyl)

phthalate (BEHP), perylene, and sulfur at the concentrations in section 6.12.2, or at concentrations appropriate to the response of the detector.

Note: Sulfur does not readily dissolve in methylene chloride, but is soluble in warm corn oil. The following procedure is suggested for preparation of the solution.

6.12.2 Weigh 8 mg sulfur and 2.5 g corn oil into a 100-mL volumetric flask and warm to dissolve the sulfur. Separately weigh 100 mg BEHP, 20 mg pentachlorophenol, and 2 mg perylene and add to flask. Bring to volume with methylene chloride and mix thoroughly.

6.12.3 Store the solution in an amber glass bottle with a fluoropolymer-lined screw cap at 0–6 °C. Protect from light. Refrigeration may cause the corn oil to precipitate. Before use, allow the solution to stand at room temperature until the corn oil dissolves, or warm slightly to aid in dissolution. Replace the solution every year, or more frequently if the response of a component changes.

6.13 Sulfur removal—Copper foil or powder (bright, non-oxidized), or tetrabutylammonium sulfite (TBA sulfite).

6.13.1 Copper foil, or powder—Fisher, Alfa Aesar 42455–18, 625 mesh, or equivalent. Cut copper foil into approximately 1-cm squares. Copper must be activated before it may be used, as described below:

6.13.1.1 Place the quantity of copper needed for sulfur removal (section 11.2.1.3) in a ground-glass-stoppered Erlenmeyer flask or bottle. Cover the foil or powder with methanol.

6.13.1.2 Add HCl dropwise (0.5–1.0 mL) while swirling, until the copper brightens.

6.13.1.3 Pour off the methanol/HCl and rinse 3 times with reagent water to remove all traces of acid, then 3 times with acetone, then 3 times with hexane.

6.13.1.4 For copper foil, cover with hexane after the final rinse. Store in a stoppered flask under nitrogen until used. For the powder, dry on a rotary evaporator or under a stream of nitrogen. Store in a stoppered flask under nitrogen until used. Inspect the copper foil or powder before each use. It must have a bright, non-oxidized appearance to be effective. Copper foil or powder that has oxidized may be reactivated using the procedure described above.

6.13.2 Tetrabutylammonium sodium sulfite (TBA sodium sulfite).

6.13.2.1 Tetrabutylammonium hydrogen sulfate, $[\text{CH}_3(\text{CH}_2)_3]_4\text{NH}\text{SO}_4$.

6.13.2.2 Sodium sulfite, Na_2SO_3 .

6.13.2.3 Dissolve approximately 3 g tetrabutylammonium hydrogen sulfate in 100 mL of reagent water in an amber bottle with fluoropolymer-lined screw cap. Extract with three 20-mL portions of hexane and discard the hexane extracts.

6.13.2.4 Add 25 g sodium sulfite to produce a saturated solution. Store at room temperature. Replace after 1 month.

6.14 DDT and endrin decomposition (breakdown) solution—Prepare a solution containing endrin at a concentration of 1 µg/mL and 4,4'-DDT at a concentration of 2 µg/mL, in isooctane or hexane. A 1-µL injection of this standard will contain 1 nanogram (ng)

of endrin and 2 ng of DDT. The concentration of the solution may be adjusted by the laboratory to accommodate other injection volumes such that the same masses of the two analytes are introduced into the instrument.

7. Calibration

7.1 Establish operating conditions equivalent to those in the footnote to Table 4 or 5 for the base/neutral or acid fraction, respectively. If a combined base/neutral/acid fraction will be analyzed, use the conditions in the footnote to Table 4. Alternative temperature program and flow rate conditions may be used. It is necessary to calibrate the GC/MS for the analytes of interest (Section 1.3) only.

7.2 Internal standard calibration.

7.2.1 Prepare calibration standards for the analytes of interest and surrogates at a minimum of five concentration levels by adding appropriate volumes of one or more stock standards to volumetric flasks. One of the calibration standards should be at a concentration at or below the ML specified in Table 1, 2, or 3, or as specified by a regulatory/control authority or in a permit. The ML value may be rounded to a whole number that is more convenient for preparing the standard, but must not exceed the ML in Table 1, 2, or 3 for those analytes which list ML values. Alternatively, the laboratory may establish a laboratory ML for each analyte based on the concentration in a nominal whole-volume sample that is equivalent to the concentration of the lowest calibration standard in a series of standards produced in the laboratory or obtained from a commercial vendor. The laboratory's ML must not exceed the ML in Table 1, 2, or 3, and the resulting calibration must meet the acceptance criteria in Section 7.2.3, based on the RSD, RSE, or R^2 . The concentrations of the other calibration standards should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system for full-scan and/or SIM operation, as appropriate. A minimum of six concentration levels is required for a second order, non-linear (e.g., quadratic; $ax^2 + bx + c = 0$) calibration (section 7.2.3). Calibrations higher than second order are not allowed. To each calibration standard or standard mixture, add a known constant volume of the internal standard solution (section 6.9), and dilute to volume with methylene chloride.

Note: The large number of analytes in Tables 1 through 3 may not be soluble or stable in a single solution; multiple solutions may be required if a large number of analytes are to be determined simultaneously.

7.2.1.1 Prior to analysis of the calibration standards, inject the DFTPP standard (Section 6.10) and adjust the scan rate of the mass spectrometer to produce a minimum of 5 mass spectra across the DFTPP GC peak. Adjust instrument conditions until the DFTPP criteria in Table 9A or 9B are met. Calculate peak tailing factors for benzidine and pentachlorophenol. Calculation of the tailing factor is illustrated in Figure 1. The tailing factor for benzidine and pentachlorophenol must be <2; otherwise, adjust instrument conditions and either

replace the column or break off a short section of the front end of the column, and repeat the test. Once the scan conditions are established, they must be used for analyses of all standards, blanks, and samples.

Note: The DFTPP spectrum may be evaluated by summing the intensities of the m/z's across the GC peak, subtracting the background at each m/z in a region of the chromatogram within 20 scans of but not including any part of, the DFTPP peak. The DFTPP spectrum may also be evaluated by fitting a Gaussian to each m/z and using the intensity at the maximum for each Gaussian or by integrating the area at each m/z and using the integrated areas. Other means may be used for evaluation of the DFTPP spectrum so long as the spectrum is not distorted to meet the criteria in Table 9A or 9B.

7.2.1.2 Analyze the mid-point combined base/neutral and acid calibration standard and enter or review the retention time, relative retention time, mass spectrum, and quantitation m/z in the data system for each analyte of interest, surrogate, and internal standard. If additional analytes (Table 3) are

to be quantified, include these analytes in the standard. The mass spectrum for each analyte must be comprised of a minimum of 2 m/z's (Tables 4 and 5); 3 to 5 m/z's assure more reliable analyte identification. Suggested quantitation m/z's are shown in Tables 4 and 5 as the primary m/z. If an interference occurs at the primary m/z, use one of the secondary m/z's or an alternate m/z. A single m/z only is required for quantitation.

7.2.1.3 For SIM operation, determine the analytes in each descriptor, the quantitation m/z for each analyte (the quantitation m/z can be the same as for full-scan operation; section 7.2.1.2), the dwell time on each m/z for each analyte, and the beginning and ending retention time for each descriptor. Analyze the verification standard in scan mode to verify m/z's and establish retention times for the analytes. There must be a minimum of two m/z's for each analyte to assure analyte identification. To maintain sensitivity, the number of m/z's in a descriptor should be limited. For example, for a descriptor with 10 m/z's and a chromatographic peak width of 5 sec, a dwell time of 100 ms at each m/z would result in

a scan time of 1 second and provide 5 scans across the GC peak. The quantitation m/z will usually be the most intense peak in the mass spectrum. The quantitation m/z and dwell time may be optimized for each analyte. The acquisition table used for SIM must take into account the mass defect (usually less than 0.2 Dalton) that can occur at each m/z monitored. Refer to the footnotes to Table 4 or 5 for establishing operating conditions and to section 7.2.1.1 for establishing scan conditions.

7.2.1.4 For combined scan and SIM operation, set up the scan segments and descriptors to meet requirements in sections 7.2.1.1–7.2.1.3. Analyze unfamiliar samples in the scan mode to assure that the analytes of interest are determined.

7.2.2 Analyze each calibration standard according to section 12 and tabulate the area at the quantitation m/z against concentration for each analyte of interest, surrogate, and internal standard. If an interference is encountered, use a secondary m/z (Table 4 or 5) for quantitation. Calculate a response factor (RF) for each analyte of interest at each concentration using Equation 1.

$$RF = \frac{(A_s \times C_{is})}{(A_{is} \times C_s)} \quad \text{Equation 1}$$

where:

A_s = Area of the characteristic m/z for the analyte of interest or surrogate.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard (µg/mL).

C_s = Concentration of the analyte of interest or surrogate (µg/mL).

7.2. Calculate the mean (average) and relative standard deviation (RSD) of the responses factors. If the RSD is less than 35%, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to fit a linear or quadratic regression of response ratios, A_s/A_{is} , vs. concentration ratios C_s/C_{is} . If used, the regression must be weighted inversely proportional to concentration. The coefficient of determination (R^2 ; Reference 10) of the weighted regression must be greater than 0.920 (this value roughly corresponds to the RSD limit of 35%). Alternatively, the relative standard error (Reference 11) may be used as an acceptance criterion. As with the RSD, the RSE must be less than 35%. If an RSE less than 35% cannot be achieved for a quadratic regression, system performance is unacceptable and the system must be adjusted and re-calibrated.

Note: Using capillary columns and current instrumentation, it is quite likely that a laboratory can calibrate the target analytes in this method and achieve a linearity metric (either RSD or RSE) well below 35%. Therefore, laboratories are permitted to use more stringent acceptance criteria for calibration than described here, for example, to harmonize their application of this method with those from other sources.

7.3 Calibration verification—The RF or calibration curve must be verified immediately after calibration and at the beginning of each 12-hour shift, by analysis of a standard at or near the concentration of the mid-point calibration standard (section 7.2.1). The standard(s) must be obtained from a second manufacturer or a manufacturer's batch prepared independently from the batch used for calibration. Traceability must be to a national standard, when available. Include the surrogates (section 6.8) in this solution. It is necessary to verify calibration for the analytes of interest (section 1.3) only.

Note: The 12-hour shift begins after the DFTPP (section 13.1) and DDT/endrin tests (if DDT and endrin are to be determined), and after analysis of the calibration verification standard. The 12-hour shift ends 12 hours later. The DFTPP, DDT/endrin, and calibration verification tests are outside of the 12-hour shift.

7.3.1 Analyze the calibration verification standard(s) beginning in section 12. Calculate the percent recovery of each analyte. Compare the recoveries for the analytes of interest against the acceptance criteria for recovery (Q) in Table 6, and the recoveries for the surrogates against the acceptance criteria in Table 8. If recovery of the analytes of interest and surrogates meet acceptance criteria, system performance is acceptable and analysis of samples may continue. If any individual recovery is outside its limit, system performance is unacceptable for that analyte.

Note: The large number of analytes in Tables 6 and 8 present a substantial probability that one or more will fail acceptance criteria when all analytes are tested simultaneously.

7.3.2 When one or more analytes fail acceptance criteria, analyze a second aliquot of the calibration verification standard and compare ONLY those analytes that failed the first test (section 7.3.1) with their respective acceptance criteria. If these analytes now pass, system performance is acceptable and analysis of samples may continue. A repeat failure of any analyte that failed the first test, however, will confirm a general problem with the measurement system. If this occurs, repair the system (section 7.2.1.1) and repeat the test (section 7.3.1), or prepare a fresh calibration standard and repeat the test. If calibration cannot be verified after maintenance or injection of the fresh calibration standard, re-calibrate the instrument.

Note: If it is necessary to perform a repeat verification test frequently; i.e., perform two tests in order to pass, it may be prudent to perform two injections in succession and review the results, rather than perform one injection, review the results, then perform the second injection if results from the first injection fail. To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between the injections.

7.3.3 Many of the analytes in Table 3 do not have QC acceptance criteria in Table 6, and some of the surrogates in Table 8 do not have acceptance criteria. If calibration is to be verified and other QC tests are to be performed for these analytes, acceptance criteria must be developed and applied. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13). Alternatively, analytes that do not have acceptance criteria in Table 6 or Table 8 may

be based on laboratory control charts, or 60 to 140% may be used.

7.3.4 Internal standard responses—Verify that detector sensitivity has not changed by comparing the response of each internal standard in the calibration verification standard (section 7.3) to the response of the respective internal standard in the midpoint calibration standard (section 7.2.1). The peak areas or heights of the internal standards in the calibration verification standard must be within 50% to 200% (1/2 to 2x) of their respective peak areas or heights in the midpoint calibration standard. If not, repeat the calibration verification test using a fresh calibration verification standard (7.3), or perform and document system repair. Subsequent to repair, repeat the calibration verification test (section 7.3.1). If the responses are still not within 50% to 200%, re-calibrate the instrument (section 7.2.2) and repeat the calibration verification test.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analysis of spiked samples and blanks to evaluate and document data quality (40 CFR 136.7). The laboratory must maintain records to document the quality of data generated. Results of ongoing performance tests are compared with established QC acceptance criteria to determine if the results of analyses meet performance requirements of this method. When results of spiked samples do not meet the QC acceptance criteria in this method, a quality control check sample (laboratory control sample; LCS) must be analyzed to confirm that the measurements were performed in an in-control mode of operation. A laboratory may develop its own performance criteria (as QC acceptance criteria), provided such criteria are as or more restrictive than the criteria in this method.

8.1.1 The laboratory must make an initial demonstration of capability (DOC) to generate acceptable precision and recovery with this method. This demonstration is detailed in Section 8.2.

8.1.2 In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options (section 1.6 and 40 CFR 136.6(b)) to improve separations or lower the costs of measurements. These options may include alternate extraction, concentration, and cleanup procedures (e.g., solid-phase extraction; rotary-evaporator concentration; column chromatography cleanup), changes in column and type of mass spectrometer (40 CFR 136.6(b)(4)(xvi)). Alternate determinative techniques, such as substitution of spectroscopic or immunoassay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than GC/MS is used, that technique must have a specificity equal to or greater than the specificity of GC/MS for the analytes of interest. The laboratory is also encouraged to participate in inter-comparison and performance evaluation studies (see section 8.10).

8.1.2.1 Each time a modification is made to this method, the laboratory is required to repeat the procedure in section 8.2. If the detection limit of the method will be affected by the change, the laboratory must demonstrate that the MDLs (40 CFR part 136, appendix B) are lower than one-third the regulatory compliance limit or the MDLs in this method, whichever are greater. If calibration will be affected by the change, the instrument must be recalibrated per section 7. Once the modification is demonstrated to produce results equivalent or superior to results produced by this method, that modification may be used routinely thereafter, so long as the other requirements in this method are met (e.g., matrix spike/matrix spike duplicate recovery and relative percent difference).

8.1.2.1.1 If SPE, or another allowed method modification, is to be applied to a specific discharge, the laboratory must prepare and analyze matrix spike/matrix spike duplicate (MS/MSD) samples (section 8.3) and LCS samples (section 8.4). The laboratory must include surrogates (section 8.7) in each of the samples. The MS/MSD and LCS samples must be fortified with the analytes of interest (Section 1.3). If the modification is for nationwide use, MS/MSD samples must be prepared from a minimum of nine different discharges (See section 8.1.2.1.2), and all QC acceptance criteria in this method must be met. This evaluation only needs to be performed once other than for the routine QC required by this method (for example it could be performed by the vendor of the SPE materials) but any laboratory using that specific material must have the results of the study available. This includes a full data package with the raw data that will allow an independent reviewer to verify each determination and calculation performed by the laboratory (see section 8.1.2.2.5, items (a)–(q)).

8.1.2.1.2 Sample matrices on which MS/MSD tests must be performed for nationwide use of an allowed modification:

- (a) Effluent from a POTW.
- (b) ASTM D5905 Standard Specification for Substitute Wastewater.
- (c) Sewage sludge, if sewage sludge will be in the permit.
- (d) ASTM D1141 Standard Specification for Substitute Ocean Water, if ocean water will be in the permit.
- (e) Untreated and treated wastewaters up to a total of nine matrix types (see <https://www.epa.gov/eg/industrial-effluent-guidelines> for a list of industrial categories with existing effluent guidelines).
 - (i) At least one of the above wastewater matrix types must have at least one of the following characteristics:
 - (A) Total suspended solids greater than 40 mg/L.
 - (B) Total dissolved solids greater than 100 mg/L.
 - (C) Oil and grease greater than 20 mg/L.
 - (D) NaCl greater than 120 mg/L.
 - (E) CaCO₃ greater than 140 mg/L.
 - (ii) Results of MS/MSD tests must meet QC acceptance criteria in Section 8.3.
- (f) A proficiency testing (PT) sample from a recognized provider, in addition to tests of the nine matrices (section 8.1.2.1.1).

8.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

8.1.2.2.1 The names, titles, and business street addresses, telephone numbers, and email addresses, of the analyst(s) that performed the analyses and modification, and of the quality control officer that witnessed and will verify the analyses and modifications.

8.1.2.2.2 A list of analytes, by name and CAS Registry Number.

8.1.2.2.3 A narrative stating reason(s) for the modifications.

8.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

- (a) Calibration (section 7).
- (b) Calibration verification (section 7).
- (c) Initial demonstration of capability (section 8.2).
- (d) Analysis of blanks (section 8.5).
- (e) Matrix spike/matrix spike duplicate analysis (section 8.3).
- (f) Laboratory control sample analysis (section 8.4).
- (g) Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:
 - (a) Sample numbers and other identifiers.
 - (b) Extraction dates.
 - (c) Analysis dates and times.
 - (d) Analysis sequence/run chronology.
 - (e) Sample weight or volume (section 10).
 - (f) Extract volume prior to each cleanup step (sections 10 and 11).
 - (g) Extract volume after each cleanup step (section 11).
 - (h) Final extract volume prior to injection (sections 10 and 12).
 - (i) Injection volume (section 12.2.3).
 - (j) Sample or extract dilution (section 12.2.3.2).
 - (k) Instrument and operating conditions.
 - (l) Column (dimensions, material, etc).
 - (m) Operating conditions (temperature program, flow rate, etc).
 - (n) Detector (type, operating conditions, etc).
 - (o) Chromatograms, mass spectra, and other recordings of raw data.
 - (p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.
 - (q) A written Standard Operating Procedure (SOP).

8.1.2.2.5 Each individual laboratory wishing to use a given modification must perform the start-up tests in section 8.1.2 (e.g., DOC, MDL), with the modification as an integral part of this method prior to applying the modification to specific discharges. Results of the DOC must meet the QC acceptance criteria in Table 6 for the analytes of interest (section 1.3), and the MDLs must be equal to or lower than the MDLs in Tables 1, 2, or 3 for the analytes of interest.

8.1.3 Before analyzing samples, the laboratory must analyze a blank to demonstrate that interferences from the analytical system, labware, and reagents are under control. Each time a batch of samples is extracted or reagents are changed, a blank

must be extracted and analyzed as a safeguard against laboratory contamination. Requirements for the blank are given in section 8.5.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze to monitor and evaluate method and laboratory performance on the sample matrix. The procedure for spiking and analysis is given in section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through analysis of a quality control check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) that the measurement system is in control. This procedure is given in section 8.4.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is given in section 8.9.

8.1.7 The large number of analytes tested in performance tests in this method present a substantial probability that one or more will fail acceptance criteria when many analytes are tested simultaneously, and a re-test is allowed if this situation should occur. If, however, continued re-testing results in further repeated failures, the laboratory must document and report the failures (e.g., as qualifiers on results), unless the failures are not required to be reported as determined by the regulatory/control authority. Results associated with a QC failure for an analyte regulated in a discharge cannot be used to demonstrate regulatory compliance. QC failures do not relieve a discharger or permittee of reporting timely results.

8.2 Initial demonstration of capability (DOC)—To establish the ability to generate acceptable recovery and precision, the laboratory must perform the DOC in sections 8.2.1 through 8.2.6 for the analytes of interest. The laboratory must also establish MDLs for the analytes of interest using the MDL procedure at 40 CFR part 136, appendix B. The laboratory's MDLs must be equal to or lower than those listed in Tables 1, 2, or 3 or lower than one third the regulatory compliance limit, whichever is greater. For MDLs not listed in Tables 4 and 5, the laboratory must determine the MDLs using the MDL procedure at 40 CFR part 136, appendix B under the same conditions used to determine the MDLs for the analytes listed in Tables 1, 2, and 3. All procedures used in the analysis, including cleanup procedures, must be included in the DOC.

8.2.1 For the DOC, a QC check sample concentrate (LCS concentrate) containing each analyte of interest (section 1.3) is prepared in a water-miscible solvent. The QC check sample concentrate must be prepared independently from those used for calibration, but may be from the same source as the second-source standard used for calibration verification (Section 7.3). The concentrate should produce concentrations of the analytes of interest in water at the midpoint of the calibration range, and may be at the same concentration as the LCS (section 8.4). Multiple solutions may be required.

Note: QC check sample concentrates are no longer available from EPA.

8.2.2 Using a pipet or micro-syringe, prepare four LCSs by adding an appropriate volume of the concentrate to each of four

aliquots of reagent water, and mix well. The volume of reagent water must be the same as the volume that will be used for the sample, blank (section 8.5), and MS/MSD (section 8.3). A volume of 1-L and a concentration of 100 µg/L were used to develop the QC acceptance criteria in Table 6. Also add an aliquot of the surrogate spiking solution (section 6.8) to the reagent-water aliquots.

8.2.3 Extract and analyze the four LCSs according to the method beginning in Section 10.

8.2.4 Calculate the average percent recovery (\bar{X}) and the standard deviation of the percent recovery (s) for each analyte using the four results.

8.2.5 For each analyte, compare s and (\bar{X}) with the corresponding acceptance criteria for precision and recovery in Table 6. For analytes in Table 3 not listed in Table 6, DOC QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13). Alternatively, acceptance criteria for analytes not listed in Table 6 may be based on laboratory control charts. If s and (\bar{X}) for all analytes of interest meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If any individual s exceeds the precision limit or any individual (\bar{X}) falls outside the range for recovery, system performance is unacceptable for that analyte.

Note: The large number of analytes in Tables 1–3 present a substantial probability that one or more will fail at least one of the acceptance criteria when many or all analytes are determined simultaneously. Therefore, the analyst is permitted to conduct a “re-test” as described in section 8.2.6.

8.2.6 When one or more of the analytes tested fail at least one of the acceptance criteria, repeat the test for only the analytes that failed. If results for these analytes pass, system performance is acceptable and analysis of samples and blanks may proceed. If one or more of the analytes again fail, system performance is unacceptable for the analytes that failed the acceptance criteria. Correct the problem and repeat the test (section 8.2). See section 8.1.7 for disposition of repeated failures.

Note: To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between this pair of tests.

8.3 Matrix spike and matrix spike duplicate (MS/MSD)—The purpose of the MS/MSD requirement is to provide data that demonstrate the effectiveness of the method as applied to the samples in question by a given laboratory, and both the data user (discharger, permittee, regulated entity, regulatory/control authority, customer, other) and the laboratory share responsibility for provision of such data. The data user should identify the sample and the analytes of interest (section 1.3) to be spiked and provide sufficient sample volume to perform MS/MSD analyses. The laboratory must, on an ongoing basis, spike at least 5% of the samples in duplicate from each discharge being monitored to assess accuracy (recovery and precision). If direction cannot be

obtained from the data user, the laboratory must spike at least one sample in duplicate per extraction batch of up to 20 samples with the analytes in Table 1. Spiked sample results should be reported only to the data user whose sample was spiked, or as requested or required by a regulatory/control authority, or in a permit.

8.3.1 If, as in compliance monitoring, the concentration of a specific analyte will be checked against a regulatory concentration limit, the concentration of the spike should be at that limit; otherwise, the concentration of the spike should be one to five times higher than the background concentration determined in section 8.3.2, at or near the midpoint of the calibration range, or at the concentration in the LCS (section 8.4) whichever concentration would be larger.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of the each analyte of interest. If necessary, prepare a new check sample concentrate (section 8.2.1) appropriate for the background concentration. Spike and analyze two additional sample aliquots, and determine the concentration after spiking (A_1 and A_2) of each analyte. Calculate the percent recoveries (P_1 and P_2) as $100(A_1 - B)/T$ and $100(A_2 - B)/T$, where T is the known true value of the spike. Also calculate the relative percent difference (RPD) between the concentrations (A_1 and A_2) as $200|A_1 - A_2|/(A_1 + A_2)$. If necessary, adjust the concentrations used to calculate the RPD to account for differences in the volumes of the spiked aliquots.

8.3.3 Compare the percent recoveries (P_1 and P_2) and the RPD for each analyte in the MS/MSD aliquots with the corresponding QC acceptance criteria in Table 6. A laboratory may develop and apply QC acceptance criteria more restrictive than the criteria in Table 6, if desired.

8.3.3.1 If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is suspect. See Section 8.1.7 for disposition of failures.

8.3.3.2 The acceptance criteria in Table 6 were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the spike to background ratio approaches 5:1 (Reference 14) and is applied to spike concentrations of 100 µg/L and higher. If spiking is performed at a concentration lower than 100 µg/L, the laboratory must use the QC acceptance criteria in Table 6, the optional QC acceptance criteria calculated for the specific spike concentration in Table 7, or optional in-house criteria (section 8.3.4). To use the acceptance criteria in Table 7: (1) Calculate recovery (X') using the equation in Table 7, substituting the spike concentration (T) for C; (2) Calculate overall precision (S') using the equation in Table 7, substituting X' for \bar{X} ; (3) Calculate the range for recovery at the spike concentration as $(100 X'/T) \pm 2.44(100 S'/T)\%$ (Reference 14). For analytes in Table 3 not listed in Table 6, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 12 and

13). Alternatively, acceptance criteria may be based on laboratory control charts.

8.3.4 After analysis of a minimum of 20 MS/MSD samples for each target analyte and surrogate, and if the laboratory chooses to develop and apply the optional in-house QC limits (Section 8.3.3), the laboratory should calculate and apply the optional in-house QC limits for recovery and RPD of future MS/MSD samples (Section 8.3). The QC limits for recovery are calculated as the mean observed recovery ± 3 standard deviations, and the upper QC limit for RPD is calculated as the mean RPD plus 3 standard deviations of the RPDs. The in-house QC limits must be updated at least every two years and re-established after any major change in the analytical instrumentation or process. If in-house QC limits are developed, at least 80% of the analytes tested in the MS/MSD must have in-house QC acceptance criteria that are tighter than those in Table 6, and the remaining analytes (those other than the analytes included in the 80%) must meet the acceptance criteria in Table 6. If an in-house QC limit for the RPD is greater than the limit in Table 6, then the limit in Table 6 must be used. Similarly, if an in-house lower limit for recovery is below the lower limit in Table 6, then the lower limit in Table 6 must be used, and if an in-house upper limit for recovery is above the upper limit in Table 6, then the upper limit in Table 6 must be used.

8.4 Laboratory control sample (LCS)—A QC check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) containing each analyte of interest (Section 1.3) and surrogate must be prepared and analyzed with each extraction batch of up to 20 samples to demonstrate acceptable recovery of the analytes of interest from a clean sample matrix.

8.4.1 Prepare the LCS by adding QC check sample concentrate (section 8.2.1) to reagent water. Include all analytes of interest (section 1.3) in the LCS. The LCS may be the same sample prepared for the DOC (section 8.2.1). The volume of reagent water must be the same as the volume used for the sample, blank (section 8.5), and MS/MSD (Section 8.3). Also add an aliquot of the surrogate spiking solution (section 6.8). The concentration of the analytes in reagent water should be the same as the concentration in the DOC (section 8.2.2).

8.4.2 Analyze the LCS prior to analysis of field samples in the extraction batch. Determine the concentration (A) of each analyte. Calculate the percent recovery (PS) as $100 (A/T)\%$, where T is the true value of the concentration in the LCS.

8.4.3 Compare the percent recovery (PS) for each analyte with its corresponding QC acceptance criterion in Table 6. For analytes of interest in Table 3 not listed in Table 6, use the QC acceptance criteria developed for the LCS (section 8.4.5), or limits based on laboratory control charts. If the recoveries for all analytes of interest fall within their respective QC acceptance criteria, analysis of blanks and field samples may proceed. If any individual PS falls outside the range, proceed according to section 8.4.4.

Note: The large number of analytes in Tables 1–3 present a substantial probability that one or more will fail the acceptance

criteria when all analytes are tested simultaneously. Because a re-test is allowed in event of failure (sections 8.1.7 and 8.4.3), it may be prudent to extract and analyze two LCSs together and evaluate results of the second analysis against the QC acceptance criteria only if an analyte fails the first test.

8.4.4 Repeat the test only for those analytes that failed to meet the acceptance criteria (PS). If these analytes now pass, system performance is acceptable and analysis of blanks and samples may proceed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, repeat the test using a fresh LCS (section 8.2.2) or an LCS prepared with a fresh QC check sample concentrate (section 8.2.1), or perform and document system repair. Subsequent to analysis of the LCS prepared with a fresh sample concentrate, or to system repair, repeat the LCS test (section 8.4). If failure of the LCS indicates a systemic problem with samples in the batch, re-extract and re-analyze the samples in the batch. See section 8.1.7 for disposition of repeated failures.

Note: To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between the pair of tests.

8.4.5 After analysis of 20 LCS samples, and if the laboratory chooses to develop and apply in-house QC limits, the laboratory should calculate and apply in-house QC limits for recovery to future LCS samples (section 8.4). Limits for recovery in the LCS should be calculated as the mean recovery ± 3 standard deviations. A minimum of 80% of the analytes tested for in the LCS must have QC acceptance criteria tighter than those in Table 6, and the remaining analytes (those other than the analytes included in the 80%) must meet the acceptance criteria in Table 6. If an in-house lower limit for recovery is lower than the lower limit in Table 6, the lower limit in Table 6 must be used, and if an in-house upper limit for recovery is higher than the upper limit in Table 6, the upper limit in Table 6 must be used. Many of the analytes and surrogates do not contain acceptance criteria. The laboratory should use 60–140% as interim acceptance criteria for recoveries of spiked analytes and surrogates that do not have recovery limits specified in Table 8, and at least 80% of the surrogates must meet the 60–140% interim criteria until in-house LCS and surrogate limits are developed. Alternatively, acceptance criteria for analytes that do not have recovery limits in Table 6 may be based on laboratory control charts. In-house QC acceptance criteria must be updated at least every two years.

8.5 Blank—A blank must be extracted and analyzed with each extraction batch to demonstrate that the reagents and equipment used for preparation and analysis are free from contamination.

8.5.1 Spike the surrogates into the blank. Extract and concentrate the blank using the same procedures and reagents used for the samples, LCS, and MS/MSD in the batch. Analyze the blank immediately after analysis of the LCS (section 8.4) and prior to analysis of the MS/MSD and samples to demonstrate freedom from contamination.

8.5.2 If an analyte of interest is found in the blank: At a concentration greater than the MDL for the analyte, at a concentration greater than one-third the regulatory compliance limit, or at a concentration greater than one-tenth the concentration in a sample in the extraction batch, *whichever is greater*, analysis of samples must be halted, and the problem corrected. If the contamination is traceable to the extraction batch, samples affected by the blank must be re-extracted and the extracts re-analyzed. If, however, continued re-testing results in repeated blank contamination, the laboratory must document and report the failures (e.g., as qualifiers on results), unless the failures are not required to be reported as determined by the regulatory/control authority. Results associated with blank contamination for an analyte regulated in a discharge cannot be used to demonstrate regulatory compliance. QC failures do not relieve a discharger or permittee of reporting timely results.

8.6 Internal standards responses.

8.6.1 Calibration verification—The responses (GC peak heights or areas) of the internal standards in the calibration verification must be within 50% to 200% ($1/2$ to $2x$) of their respective responses in the mid-point calibration standard. If they are not, repeat the calibration verification (Section 7.4) test or perform and document system repair. Subsequent to repair, repeat the calibration verification. If the responses are still not within 50% to 200%, re-calibrate the instrument (Section 7) and repeat the calibration verification test.

8.6.2 Samples, blanks, LCSs, and MS/MSDs—The responses (GC peak heights or areas) of each internal standard in each sample, blank, and MS/MSD must be within 50% to 200% ($1/2$ to $2x$) of its respective response in the LCS for the extraction batch. If, as a group, all internal standards are not within this range, perform and document system repair, repeat the calibration verification (section 8.4), and re-analyze the affected samples. If a single internal standard is not within the 50% to 200% range, use an alternate internal standard for quantitation of the analyte referenced to the affected internal standard. It may be necessary to use the data system to calculate a new response factor from calibration data for the alternate internal standard/analyte pair. If an internal standard fails the 50–200% criteria and no analytes are detected in the sample, ignore the failure or report it if required by the regulatory/control authority.

8.7 Surrogate recoveries—The laboratory must evaluate surrogate recovery data in each sample against its in-house surrogate recovery limits. The laboratory may use 60–140% as interim acceptance criteria for recoveries for surrogates not listed in Table 8. At least 80% of the surrogates must meet the 60–140% interim criteria until in-house limits are developed. Alternatively, surrogate recovery limits may be developed from laboratory control charts, but such limits must be at least as restrictive as those in Table 8. Spike the surrogates into all samples, blanks, LCSs, and MS/MSDs. Compare surrogate recoveries against the QC acceptance criteria in Table 8 and/or those developed in section 7.3.3 or 8.4.5. If any

recovery fails its criteria, attempt to find and correct the cause of the failure. See section 8.1.7 for disposition of failures.

8.8 DDT and endrin decomposition (breakdown)—If DDT and/or endrin are to be analyzed using this method, the DDT/endrin decomposition test in section 13.8 must be performed to reliably quantify these two pesticides.

8.9 As part of the QC program for the laboratory, control charts or statements of accuracy for wastewater samples must be assessed and records maintained (40 CFR 136.7(c)(1)(viii)). After analysis of five or more spiked wastewater samples as in section 8.3, calculate the average percent recovery (P_x) and the standard deviation of the percent recovery (sp). Express the accuracy assessment as a percent interval from $P_x - 2sp$ to $P_x + 2sp$. For example, if $P_x = 90\%$ and $sp = 10\%$, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each analyte on a regular basis (e.g., after each 5–10 new accuracy measurements). If desired, statements of accuracy for laboratory performance, independent of performance on samples, may be developed using LCSs.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Collect samples as grab samples in amber or clear glass bottles, or in refrigerated bottles using automatic sampling equipment. If clear glass is used, protect samples from light. Collect 1-L of ambient waters, effluents, and other aqueous samples. If the sensitivity of the analytical system is sufficient, a smaller volume (e.g., 250 mL), but no less than 100 mL, may be used. Conventional sampling practices (Reference 15) should be followed, except that the bottle must not be pre-rinsed with sample before collection. Automatic sampling equipment must be as free as possible of polyvinyl chloride or other tubing or other potential sources of contamination. If needed, collect additional sample(s) for the MS/MSD (section 8.3).

9.2 Ice or refrigerate samples at $\leq 6^\circ\text{C}$ from the time of collection until extraction, but do not freeze. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. Any method suitable for field use may be employed to test for residual chlorine (Reference 16). Add more sodium sulfate if 80 mg/L is insufficient but do not add excess sodium thiosulfate. If sodium thiosulfate interferes in the determination of the analytes, an alternate preservative (e.g., ascorbic acid or sodium sulfite) may be used. If preservative has been added, shake the sample vigorously for one minute. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 All samples must be extracted within 7 days of collection and sample extracts must be analyzed within 40 days of extraction.

10. Extraction

10.1 This section contains procedures for separatory funnel liquid-liquid extraction (SFLLE) and continuous liquid-liquid extraction (CLLE). SFLLE is faster, but may not be as effective as CLLE for recovery of polar analytes such as phenol. SFLLE is labor intensive and may result in formation of emulsions that are difficult to break. CLLE is less labor intensive, avoids emulsion formation, but requires more time (18–24 hours) and more hood space, and may require more solvent. The procedures assume base-neutral extraction followed by acid extraction. For some matrices and analytes of interest, improved results may be obtained by acid-neutral extraction followed by base extraction. A single acid or base extraction may also be performed. If an extraction scheme alternate to base-neutral followed by acid extraction is used, all QC tests must be performed and all QC acceptance criteria must be met with that extraction scheme as an integral part of this method. Solid-phase extraction (SPE) may be used provided requirements in section 8.1.2 are met.

10.2 Separatory funnel liquid-liquid extraction (SFLLE) and extract concentration.

10.2.1 The SFLLE procedure below assumes a sample volume of 1 L. When a different sample volume is extracted, adjust the volume of methylene chloride accordingly.

10.2.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into the separatory funnel. Pipet the surrogate standard spiking solution (section 6.8) into the separatory funnel. If the sample will be used for the LCS or MS or MSD, pipet the appropriate check sample concentrate (section 8.2.1 or 8.3.2) into the separatory funnel. Mix well. Check the pH of the sample with wide-range pH paper and adjust to pH 11–13 with sodium hydroxide solution.

10.2.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for approximately 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool or phase-separation paper, salting, centrifugation, or other physical methods. Collect the methylene chloride extract in a flask. If the emulsion cannot be broken (recovery of $<80\%$ of the methylene chloride), transfer the sample, solvent, and emulsion into a continuous extractor and proceed as described in section 10.3.

10.2.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second

time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.2.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60 mL aliquots of methylene chloride. Collect and combine the extracts in a flask in the same manner as the base/neutral extracts.

Note: Base/neutral and acid extracts may be combined for concentration and analysis provided all QC tests are performed and all QC acceptance criteria met for the analytes of interest with the combined extract as an integral part of this method, and provided that the analytes of interest are as reliably identified and quantified as when the extracts are analyzed separately. If doubt exists as to whether identification and quantitation will be affected by use of a combined extract, the fractions must be analyzed separately.

10.2.6 For each fraction or the combined fractions, assemble a Kuderna-Danish (K–D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K–D concentrator so long as the requirements in section 8.2 are met.

10.2.7 For each fraction or the combined fractions, pour the extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K–D concentrator. Rinse the Erlenmeyer flask and column with 20–30 mL of methylene chloride to complete the quantitative transfer.

10.2.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction (section 10.2.7). Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath ($60\text{--}65^\circ\text{C}$) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL or other determined amount, remove the K–D apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. If the sample will be cleaned up, reserve the K–D apparatus for concentration of the cleaned up extract. Adjust the volume to 5 mL with methylene chloride and proceed to section 11 for cleanup; otherwise, further concentrate the extract for GC/MS analysis per section 10.2.9 or 10.2.10.

10.2.9 Micro Kuderna-Danish concentration—Add another one or two clean boiling chips to the concentrator tube for each fraction and attach a two-ball micro-Snyder column. Pre-wet the Snyder column

by adding about 0.5 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65 °C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5–10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 1 mL or other determined amount, remove the K–D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of or methylene chloride. Adjust the final volume to 1.0 mL or a volume appropriate to the sensitivity desired (*e.g.*, to meet lower MDLs or for selected ion monitoring). Record the volume, stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to fluoropolymer-lined screw-cap vials and labeled base/neutral or acid fraction as appropriate. Mark the level of the extract on the vial so that solvent loss can be detected.

10.2.10 Nitrogen evaporation and solvent exchange—Extracts may be concentrated for analysis using nitrogen evaporation in place of micro K–D concentration (section 10.2.9). Extracts that have been cleaned up using sulfur removal (section 11.2) and are ready for analysis are exchanged into methylene chloride.

10.2.10.1 Transfer the vial containing the sample extract to the nitrogen evaporation (blowdown) device (section 5.8). Lower the vial into the water bath and begin concentrating. If the more volatile analytes (section 1.2) are to be concentrated, use room temperature for concentration; otherwise, a slightly elevated (*e.g.*, 30–45 °C) may be used. During the solvent evaporation process, keep the solvent level below the water level of the bath and do not allow the extract to become dry. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed. A large vortex in the solvent may cause analyte loss.

10.2.10.2 Extracts to be solvent exchanged—When the volume of the liquid is approximately 200 µL, add 2 to 3 mL of methylene chloride and continue concentrating to approximately 100 µL. Repeat the addition of solvent and concentrate once more. Adjust the final extract volume to be consistent with the volume extracted and the sensitivity desired.

10.2.10.3 For extracts that have been cleaned up by GPC and that are to be concentrated to a nominal volume of 1 mL, adjust the final volume to compensate the GPC loss. For a 50% GPC loss, concentrate the extract to 1/2000 of the volume extracted. For example, if the volume extracted is 950 mL, adjust the final volume to 0.48 mL. For extracts that have not been cleaned up by GPC and are to be concentrated to a nominal volume of 1.0 mL, adjust the final extract volume to 1/1000 of the volume extracted. For example, if the volume extracted is 950

mL, adjust the final extract volume to 0.95 mL. Alternative means of compensating the loss during GPC are acceptable so long as they produce results as accurate as results produced using the procedure detailed in this Section. An alternative final volume may be used, if desired, and the calculations adjusted accordingly.

Note: The difference in the volume fraction for an extract cleaned up by GPC accounts for the loss in GPC cleanup. Also, by preserving the ratio between the volume extracted and the final extract volume, the concentrations and detection limits do not need to be adjusted for differences in the volume extracted and the extract volume.

10.2.11 Transfer the concentrated extract to a vial with fluoropolymer-lined cap. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for GC analysis. If GC analysis will not be performed on the same day, store the vial in the dark at ≤6 °C. Analyze the extract by GC/MS per the procedure in section 12.

10.2.12 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to an appropriately sized graduated cylinder. For sample volumes on the order of 1000 mL, record the sample volume to the nearest 10 mL; for sample volumes on the order of 100 mL, record the volume to the nearest 1 mL. Sample volumes may also be determined by weighing the container before and after filling to the mark with water.

10.3 Continuous liquid/liquid extraction (CLLE).

Note: With CLLE, phenol, 2,4-dimethyl phenol, and some other analytes may be preferentially extracted into the base-neutral fraction. Determine an analyte in the fraction in which it is identified and quantified most reliably. Also, the short-chain phthalate esters (*e.g.*, dimethyl phthalate, diethyl phthalate) and some other compounds may hydrolyze during prolonged exposure to basic conditions required for continuous extraction, resulting in low recovery of these analytes. When these analytes are of interest, their recovery may be improved by performing the acid extraction first.

10.3.1 Use CLLE when experience with a sample from a given source indicates an emulsion problem, or when an emulsion is encountered during SFLLE. CLLE may be used for all samples, if desired.

10.3.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH 11–13 with sodium hydroxide solution. Transfer the sample to the continuous extractor. Pipet surrogate standard spiking solution (section 6.8) into the sample. If the sample will be used for the LCS or MS or MSD, pipet the appropriate check sample concentrate (section 8.2.1 or 8.3.2) into the extractor. Mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor.

10.3.3 Repeat the sample bottle rinse with an additional 50–100 mL portion of methylene chloride and add the rinse to the extractor.

10.3.4 Add a suitable volume of methylene chloride to the distilling flask (generally 200–500 mL), add sufficient reagent water to ensure proper operation, and extract for 18–24 hours. A shorter or longer extraction time may be used if all QC acceptance criteria are met. Test and, if necessary, adjust the pH of the water during the second or third hour of the extraction. After extraction, allow the apparatus to cool, then detach the distilling flask. Dry, concentrate, and seal the extract per sections 10.2.6 through 10.2.11. See the note at section 10.2.5 regarding combining extracts of the base/neutral and acid fractions.

10.3.5 Charge the distilling flask with methylene chloride and attach it to the continuous extractor. Carefully, while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Extract for 18–24 hours. A shorter or longer extraction time may be used if all QC acceptance criteria are met. Test and, if necessary, adjust the pH of the water during the second or third hour of the extraction. After extraction, allow the apparatus to cool, then detach the distilling flask. Dry, concentrate, and seal the extract per sections 10.2.6 through 10.2.11. Determine the sample volume per section 10.2.12.

11. Extract Cleanup

Note: Cleanup may not be necessary for relatively clean samples (*e.g.*, treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the laboratory may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the laboratory must demonstrate that the requirements of section 8.1.2 can be met using the cleanup procedure as an integral part of this method.

11.1 Gel permeation chromatography (GPC).

11.1.1 Calibration.

11.1.1.1 Load the calibration solution (section 6.12) into the sample loop.

11.1.1.2 Inject the calibration solution and record the signal from the detector. The elution pattern will be corn oil, bis(2-ethylhexyl) phthalate, pentachlorophenol, perylene, and sulfur.

11.1.1.3 Set the “dump time” to allow >85% removal of the corn oil and >85% collection of the phthalate.

11.1.1.4 Set the “collect time” to the peak minimum between perylene and sulfur.

11.1.1.5 Verify calibration with the calibration solution after every 20 or fewer extracts. Calibration is verified if the recovery of the pentachlorophenol is greater than 85%. If calibration is not verified, recalibrate using the calibration solution, and re-extract and clean up the preceding extracts using the calibrated GPC system.

11.1.2 Extract cleanup—GPC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 0.5 g of high molecular weight material in a 5-mL extract. If the extract is known or expected to contain more than 0.5 g, the extract is split into fractions for GPC and the fractions are combined after elution from the column. The solids content of the extract may be obtained

gravimetrically by evaporating the solvent from a 50- μ L aliquot.

11.1.2.1 Filter the extract or load through the filter holder to remove particulates. Load the extract into the sample loop. The maximum capacity of the column is 0.5–1.0 g. If necessary, split the extract into multiple aliquots to prevent column overload.

11.1.2.2 Elute the extract using the calibration data determined in Section 11.1.1. Collect the eluate in the K–D apparatus reserved in section 10.2.8.

11.1.3 Concentrate the cleaned up extract per sections 10.2.8 and 10.2.9 or 10.2.10.

11.1.4 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

11.1.5 If a particularly dirty extract is encountered, run a methylene chloride blank through the system to check for carry-over.

11.2 Sulfur removal.

Note: Separate procedures using copper or TBA sulfite are provided in this section for sulfur removal. They may be used separately or in combination, if desired.

11.2.1 Removal with copper (Reference 17).

Note: If an additional compound (Table 3) is to be determined; sulfur is to be removed; copper will be used for sulfur removal; and a sulfur matrix is known or suspected to be present, the laboratory must demonstrate that the additional compound can be successfully extracted and treated with copper in the sulfur matrix. Some of the additional compounds (Table 3) are known not to be amenable to sulfur removal with copper (*e.g.* Atrazine and Diazinon).

11.2.1.1 Quantitatively transfer the extract from section 10.2.8 to a 40- to 50-mL flask or bottle. If there is evidence of water in the concentrator tube after the transfer, rinse the tube with small portions of hexane:acetone (40:60) and add to the flask or bottle. Mark and set aside the concentrator tube for use in re-concentrating the extract.

11.2.1.2 Add 10–20 g of granular anhydrous sodium sulfate to the flask. Swirl to dry the extract.

11.2.1.3 Add activated copper (section 6.13.1.4) and allow to stand for 30–60 minutes, swirling occasionally. If the copper does not remain bright, add more and swirl occasionally for another 30–60 minutes.

11.2.1.4 After drying and sulfur removal, quantitatively transfer the extract to a nitrogen-evaporation vial or tube and proceed to section 10.2.10 for nitrogen evaporation and solvent exchange, taking care to leave the sodium sulfate and copper in the flask.

11.2.2 Removal with TBA sulfite.

11.2.2.1 Using small volumes of hexane, quantitatively transfer the extract to a 40- to 50-mL centrifuge tube with fluoropolymer-lined screw cap.

11.2.2.2 Add 1–2 mL of TBA sulfite reagent (section 6.13.2.4), 2–3 mL of 2-propanol, and approximately 0.7 g of sodium sulfite (section 6.13.2.2) crystals to the tube. Cap and shake for 1–2 minutes. If the sample is colorless or if the initial color is

unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 0.5 g portions until a solid residue remains after repeated shaking.

11.2.2.3 Add 5–10 mL of reagent water and shake for 1–2 minutes. Centrifuge to settle the solids.

11.2.2.4 Quantitatively transfer the hexane (top) layer through a small funnel containing a few grams of granular anhydrous sodium sulfate to a nitrogen-evaporation vial or tube and proceed to section 10.2.10 for nitrogen evaporation and solvent exchange.

12. Gas Chromatography/Mass Spectrometry

12.1 Establish the operating conditions in Table 4 or 5 for analysis of a base/neutral or acid extract, respectively. For analysis of a combined extract (section 10.2.5, note), use the operating conditions in Table 4 MDLs and MLs for the analytes are given in Tables 1, 2, and 3. Retention times for many of the analytes are given in Tables 4 and 5. Examples of the separations achieved are shown in Figure 2 for the combined extract. Alternative columns or chromatographic conditions may be used if the requirements of section 8.2 are met. Verify system performance per section 13.

12.2 Analysis of a standard or extract.

12.2.1 Bring the standard or concentrated extract (section 10.2.9 or 10.2.11) to room temperature and verify that any precipitate has redissolved. Verify the level on the extract and bring to the mark with solvent if required.

12.2.2 Add the internal standard solution (section 6.9) to the extract. Mix thoroughly.

12.2.3 Inject an appropriate volume of the sample extract or standard solution using split, splitless, solvent purge, large-volume, or on-column injection. If the sample is injected manually the solvent-flush technique should be used. The injection volume depends upon the technique used and the ability to meet MDLs or reporting limits for regulatory compliance. Injected volumes must be the same for standards and sample extracts. Record the volume injected to two significant figures.

12.2.3.1 Start the GC column oven program upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after benzo(ghi)perylene elutes for the base/neutral or combined fractions, or after pentachlorophenol elutes for the acid fraction. Return the column to the initial temperature for analysis of the next standard solution or extract.

12.2.3.2 If the concentration of any analyte of interest exceeds the calibration range, either extract and analyze a smaller sample volume, or dilute and analyze the diluted extract after bringing the concentrations of the internal standards to the levels in the undiluted extract.

12.2.4 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When standards and

extracts are not being used for analyses, store them refrigerated at $\leq 6^\circ\text{C}$ protected from light in screw-cap vials equipped with unpierced fluoropolymer-lined septa.

13. Performance Tests

13.1 At the beginning of each 12-hour shift during which standards or extracts will be analyzed, perform the tests in sections 13.2–13.4 to verify system performance. If an extract is concentrated for greater sensitivity (*e.g.*, by SIM), all tests must be performed at levels consistent with the reduced extract volume.

13.2 DFTPP—Inject the DFTPP standard (section 6.10) and verify that the criteria for DFTPP in section 7.2.1.1 and Table 9A (Reference 18) for a quadrupole MS, or Table 9B (Reference 19) for a time-of-flight MS, are met.

13.3 GC resolution—The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (*e.g.*, benzo(b)fluoranthene and benzo(k)fluoranthene). Sufficient gas chromatographic resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights.

13.4 Calibration verification—Verify calibration per sections 7.3 and Table 6.

13.5 Peak tailing—Verify the tailing factor specifications are met per Section 7.2.1.1.

13.6 Laboratory control sample and blank—Analyze the extracts of the LCS and blank at the beginning of analyses of samples in the extraction batch (section 3.1). The LCS must meet the requirements in section 8.4, and the blank must meet the requirements in section 8.5 before sample extracts may be analyzed.

13.7 Analysis of DFTPP, the DDT/Endrin decomposition test (if used), the LCS, and the blank are outside of the 12-hour analysis shift (section 3.1). The total time for DFTPP, DDT/Endrin, the LCS, the blank, and the 12-hour shift must not exceed 15 hours.

13.8 Decomposition of DDT and endrin—If DDT and/or endrin are to be determined, this test must be performed prior to calibration verification (section 13.4). The QC acceptance criteria (section 13.8.3) must be met before analyzing samples for DDE and/or Endrin. DDT decomposes to DDE and DDD. Endrin decomposes to endrin aldehyde and endrin ketone.

13.8.1 Inject 1 μ L of the DDT and endrin decomposition solution (section 6.14). As noted in section 6.14, other injection volumes may be used as long as the concentrations of DDT and endrin in the solution are adjusted to introduce the masses of the two analytes into the instrument that are listed in section 6.14.

13.8.2 Measure the areas of the peaks for DDT, DDE, DDD, Endrin, Endrin aldehyde, and Endrin ketone. Calculate the percent breakdown as shown in the equations below:

$$\% \text{ breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD + DDE)}}{\text{sum of all peak areas (DDT + DDE + DDD)}} \times 100$$

% breakdown of Endrin

$$= \frac{\text{sum of degradation peak areas (Endrin aldehyde + Endrin ketone)}}{\text{sum of all peak areas (Endrin + Endrin aldehyde + Endrin ketone)}} \times 100$$

13.8.3 Both the % breakdown of DDT and of Endrin must be less than 20%, otherwise the system is not performing acceptably for DDT and endrin. In this case, repair the GC column system that failed and repeat the performance tests (sections 13.2 to 13.6) until the specification is met.

Note: DDT and endrin decomposition are usually caused by accumulation of particulates in the injector and in the front end of the column. Cleaning and silanizing the injection port liner, and breaking off a short section of the front end of the column will usually eliminate the decomposition problem. Either of these corrective actions may affect retention times, GC resolution, and calibration linearity.

14. Qualitative Identification

14.1 Identification is accomplished by comparison of data from analysis of a sample or blank with data stored in the GC/MS data system (sections 5.6.5 and 7.2.1.2). Identification of an analyte is confirmed per sections 14.1.1 through 14.1.4.

14.1.1 The signals for the quantitation and secondary m/z's stored in the data system for each analyte of interest must be present and must maximize within the same two consecutive scans.

14.1.2 The retention time for the analyte should be within ± 10 seconds of the analyte

in the calibration verification run at the beginning of the shift (section 7.3 or 13.4).

Note: Retention time windows other than ± 10 seconds may be appropriate depending on the performance of the gas chromatograph or observed retention time drifts due to certain types of matrix effects. Relative retention time (RRT) may be used as an alternative to absolute retention times if retention time drift is a concern. RRT is a unitless quantity (see Sec. 22.2), although some procedures refer to "RRT units" in providing the specification for the agreement between the RRT values in the sample and the calibration verification or other standard. When significant retention time drifts are observed, dilutions or spiked samples may help the analyst determine the effects of the matrix on elution of the target analytes and to assist in qualitative identification.

14.1.3 Either the background corrected EICP areas, or the corrected relative intensities of the mass spectral peaks at the GC peak maximum, must agree within 50% to 200% (1/2 to 2 times) for the quantitation and secondary m/z's in the reference mass spectrum stored in the data system (section 7.2.1.2), or from a reference library. For example, if a peak has an intensity of 20% relative to the base peak, the analyte is identified if the intensity of the peak in the sample is in the range of 10% to 40% of the

base peak. If identification is ambiguous, an experienced spectrometrist (section 1.7) must determine the presence or absence of the compound.

14.2 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different gas chromatographic retention times. Sufficient gas chromatographic resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

15. Calculations

15.1 When an analyte has been identified, quantitation of that analyte is based on the integrated abundance from the EICP of the primary characteristic m/z in Table 4 or 5. Calculate the concentration in the extract using the response factor (RF) determined in Section 7.2.2 and Equation 2. If the concentration of an analyte exceeds the calibration range, dilute the extract by the minimum amount to bring the concentration into the calibration range, and re-analyze the extract. Determine a dilution factor (DF) from the amount of the dilution. For example, if the extract is diluted by a factor of 2, DF = 2.

$$C_{\text{ex}} (\mu\text{g/mL}) = \frac{A_s \times C_{\text{is}}}{A_{\text{is}} \times \text{RF}}$$

Equation 2

where:

C_{ex} = Concentration of the analyte in the extract, in $\mu\text{g/mL}$, and the other terms are as defined in section 7.2.2.

Calculate the concentration of the analyte in the sample using the concentration in the extract, the extract volume, the sample

volume, and the dilution factor, per Equation 3:

$$C_{\text{samp}} (\mu\text{g/L}) = \frac{C_{\text{ex}} \times V_{\text{ex}} \times \text{DF}}{V_s}$$

Equation 3

where:

C_{samp} = Concentration of the analyte in the sample

C_{ex} = Concentration of the analyte in the extract, in $\mu\text{g/mL}$

V_{ex} = Volume of extract (mL)

V_s = Volume of sample (L)

DF = Dilution factor

15.2 Reporting of results. As noted in section 1.4.1, EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described here are focused on such monitoring needs and may not be relevant to other uses of the method.

15.2.1 Report results for wastewater samples in $\mu\text{g/L}$ without correction for recovery. (Other units may be used if required by a permit.) Report all QC data with the sample results.

15.2.2 Reporting level. Unless specified otherwise by a regulatory authority or in a discharge permit, results for analytes that meet the identification criteria are reported

down to the concentration of the ML established by the laboratory through calibration of the instrument (see section 7.3.2 and the glossary for the derivation of the ML). EPA considers the terms "reporting limit," "quantitation limit," "limit of quantitation," and "minimum level" to be synonymous.

15.2.2.1 Report a result for each analyte in each field sample or QC standard at or above the ML to 3 significant figures. Report a result for each analyte found in each field sample or QC standard below the ML as "ML" where ML is the concentration of the analyte at the ML, or as required by the regulatory/control authority or permit. Report a result for each analyte in a blank at or above the MDL to 2 significant figures. Report a result for each analyte found in a blank below the MDL as "MDL," where MDL is the concentration of the analyte at the MDL, or as required by the regulatory/control authority or permit.

15.2.2.2 In addition to reporting results for samples and blanks separately, the concentration of each analyte in a blank associated with the sample may be subtracted from the result for that sample, but only if requested or required by a regulatory authority or in a permit. In this case, both the sample result and the blank results must be reported together.

15.2.2.3 Report a result for an analyte found in a sample or extract that has been diluted at the least dilute level at which the area at the quantitation m/z is within the calibration range (*i.e.*, above the ML for the analyte) and the MS/MSD recovery and RPD are within their respective QC acceptance criteria (Table 6). This may require reporting results for some analytes from different analyses.

15.2.3 Results from tests performed with an analytical system that is not in control (*i.e.*, that does not meet acceptance criteria for any QC test in this method) must be documented and reported (*e.g.*, as a qualifier on results), unless the failure is not required to be reported as determined by the regulatory/control authority. Results associated with a QC failure cannot be used to demonstrate regulatory compliance. QC failures do not relieve a discharger or permittee of reporting timely results. If the holding time would be exceeded for a re-analysis of the sample, the regulatory/control authority should be consulted for disposition.

16. Method Performance

16.1 The basic version of this method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5–1300 $\mu\text{g/L}$ (Reference 2). Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

16.2 As noted in section 1.1, this method was validated through an interlaboratory study in the early 1980s. However, the fundamental chemistry principles used in this method remain sound and continue to apply.

16.3 A chromatogram of the combined acid/base/neutral calibration standard is shown in Figure 2.

17. Pollution Prevention

17.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operations. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, the laboratory should use pollution prevention techniques to address waste generation. When wastes cannot be reduced at the source, the Agency recommends recycling as the next best option.

17.2 The analytes in this method are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards. This method utilizes significant quantities of methylene chloride. Laboratories are encouraged to recover and recycle this and other solvents during extract concentration.

17.3 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW., Washington DC 20036, 202–872–4477.

18. Waste Management

18.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. An overview of requirements can be found in *Environmental Management Guide for Small Laboratories* (EPA 233–B–98–001).

18.2 Samples at $\text{pH} < 2$, or $\text{pH} > 12$, are hazardous and must be handled and disposed of as hazardous waste, or neutralized and disposed of in accordance with all federal, state, and local regulations. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, see "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in section 17.3.

18.3 Many analytes in this method decompose above 500 °C. Low-level waste

such as absorbent paper, tissues, and plastic gloves may be burned in an appropriate incinerator. Gross quantities of neat or highly concentrated solutions of toxic or hazardous chemicals should be packaged securely and disposed of through commercial or governmental channels that are capable of handling these types of wastes.

18.4 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel and Less is Better—Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW., Washington, DC 20036, 202–872–4477.

19. References

1. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977.
2. "EPA Method Study 30, Method 625, Base/Neutrals, Acids, and Pesticides," EPA 600/4–84–053, National Technical Information Service, PB84–206572, Springfield, Virginia 22161, June 1984.
3. 40 CFR part 136, appendix B.
4. Olynyk, P., Budde, W.L. and Eichelberger, J.W. "Method Detection Limit for Methods 624 and 625," Unpublished report, May 14, 1980.
5. Annual Book of ASTM Standards, Volume 11.02, D3694–96, "Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.
6. Solutions to Analytical Chemistry Problems with Clean Water Act Methods, EPA 821–R–07–002, March 2007.
7. "Carcinogens-Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77–206, August 1977.
8. "OSHA Safety and Health Standards, General Industry," (29 CFR part 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
9. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 7th Edition, 2003.
10. Johnson, R.A., and Wichern, D.W., "Applied Multivariate Statistical Analysis," 3rd edition, Prentice Hall, Englewood Cliffs, NJ, 1992.
11. 40 CFR 136.6(b)(4)(x).
12. 40 CFR 136.6(b)(2)(i).
13. Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water (EPA–821–B–98–003) March 1999.
14. Provost, L.P. and Elder, R.S. "Interpretation of Percent Recovery Data," American Laboratory, 15, 58–63 (1983). (The value 2.44 used in the equation in section 8.3.3 is two times the value 1.22 derived in this report.)

15. ASTM Annual Book of Standards, Part 31, D3370–76. “Standard Practices for Sampling Water,” American Society for Testing and Materials, Philadelphia.
16. 40 CFR 136.3(a), Table IB, Chlorine—Total Residual.
17. “Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples,” EPA–600/8–80–038, U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina.
18. Eichelberger, J.W., Harris, L.E., and Budde, W.L. “Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry,” Analytical Chemistry, 47, 995 (1975).
19. Letter of approval of acceptance criteria for DFTPP for time-of-flight mass spectrometers from William A. Telliard and Herb Brass of EPA to Jack Cochran of LECO Corporation, February 9, 2005.
20. Tables

TABLE 1—NON PESTICIDE/PCB BASE/NEUTRAL EXTRACTABLES ¹

Analyte	CAS registry	MDL ⁴ (ug/L)	ML ⁵ (ug/L)
Acenaphthene	83–32–9	1.9	5.7
Acenaphthylene	208–96–8	3.5	10.5
Anthracene	120–12–7	1.9	5.7
Benzidine ²	92–87–5	44	132
Benzo(a)anthracene	56–55–3	7.8	23.4
Benzo(a)pyrene	50–32–8	2.5	7.5
Benzo(b)fluoranthene	205–99–2	4.8	14.4
Benzo(k)fluoranthene	207–08–9	2.5	7.5
Benzo(ghi)perylene	191–24–2	4.1	12.3
Benzyl butyl phthalate	85–68–7	2.5	7.5
bis(2-Chloroethoxy)methane	111–91–1	5.3	15.9
bis(2-Ethylhexyl)phthalate	117–81–7	2.5	7.5
bis(2-Chloroisopropyl) ether (2,2'-Oxybis[1-chloropropane])	108–60–1	5.7	17.1
4-Bromophenyl phenyl ether	101–55–3	1.9	5.7
2-Chloronaphthalene	91–58–7	1.9	5.7
4-Chlorophenyl phenyl ether	7005–72–3	4.2	12.6
Chrysene	218–01–9	2.5	7.5
Dibenz(a,h)anthracene	53–70–3	2.5	7.5
Di- <i>n</i> -butylphthalate	84–74–2	2.5	7.5
3,3'-Dichlorobenzidine	91–94–1	16.5	49.5
Diethyl phthalate	84–66–2	1.9	5.7
Dimethyl phthalate	131–11–3	1.6	4.8
2,4-Dinitrotoluene	121–14–2	5.7	17.1
2,6-Dinitrotoluene	606–20–2	1.9	5.7
Di- <i>n</i> -octylphthalate	117–84–0	2.5	7.5
Fluoranthene	206–44–0	2.2	6.6
Fluorene	86–73–7	1.9	5.7
Hexachlorobenzene	118–74–1	1.9	5.7
Hexachlorobutadiene	87–68–3	0.9	2.7
Hexachloroethane	67–72–1	1.6	4.8
Indeno(1,2,3- <i>cd</i>)pyrene	193–39–5	3.7	11.1
Isophorone	78–59–1	2.2	6.6
Naphthalene	91–20–3	1.6	4.8
Nitrobenzene	98–95–3	1.9	5.7
N-Nitrosodi- <i>n</i> -propylamine ³	621–64–7	—	—
Phenanthrene	85–01–8	5.4	16.2
Pyrene	129–00–0	1.9	5.7
1,2,4-Trichlorobenzene	120–82–1	1.9	5.7

¹ All analytes in this table are Priority Pollutants (40 CFR part 423, appendix A).

² Included for tailing factor testing.

³ See section 1.2.

⁴ MDL values from the 1984 promulgated version of Method 625.

⁵ ML = Minimum Level—see Glossary for definition and derivation.

TABLE 2—ACID EXTRACTABLES ¹

Analyte	CAS registry	MDL ³ (ug/L)	ML ⁴ (ug/L)
4-Chloro-3-methylphenol	59–50–7	3.0	9.0
2-Chlorophenol	95–57–8	3.3	9.9
2,4-Dichlorophenol	120–83–2	2.7	8.1
2,4-Dimethylphenol	105–67–9	2.7	8.1
2,4-Dinitrophenol	51–28–5	42	126
2-Methyl-4,6-dinitrophenol	534–52–1	24	72
2-Nitrophenol	88–75–5	3.6	10.8
4-Nitrophenol	100–02–7	2.4	7.2
Pentachlorophenol ²	87–86–5	3.6	10.8
Phenol	108–95–2	1.5	4.5
2,4,6-Trichlorophenol	88–06–2	2.7	8.1

¹ All analytes in this table are Priority Pollutants (40 CFR part 423, appendix A).

² See section 1.2; included for tailing factor testing.³ MDL values from the 1984 promulgated version of Method 625.⁴ ML = Minimum Level—see Glossary for definition and derivation.TABLE 3—ADDITIONAL EXTRACTABLE ANALYTES ^{1, 2}

Analyte	CAS registry	MDL ⁷ (ug/L)	ML ⁸ (ug/L)
Acetophenone	98–86–2
2-Acetylaminofluorene	53–96–3
1-Acetyl-2-thiourea	591–08–2
Alachlor	15972–60–8
Aldrin ³	309–00–2	1.9	5.7
Ametryn	834–12–8
2-Aminoanthraquinone	117–79–3
Aminoazobenzene	60–09–3
4-Aminobiphenyl	92–67–1
3-Amino-9-ethylcarbazole	132–32–1
Anilazine	101–05–3
Aniline	62–53–3
o-Anisidine	90–04–0
Aramite	140–57–8
Atraton	1610–17–9
Atrazine	1912–24–9
Azinphos-methyl	86–50–0
Barban	101–27–9
Benzanthrone	82–05–3
Benzenethiol	108–98–5
Benzoic acid	65–85–0
2,3-Benzofluorene	243–17–4
p-Benzoquinone	106–51–4
Benzyl alcohol	100–51–6
alpha-BHC ^{3,4}	319–84–6
beta-BHC ³	319–85–7	3.1	9.3
gamma-BHC (Lindane) ^{3,4}	58–89–8	4.2	12.6
delta-BHC ³	319–86–8
Biphenyl	92–52–4
Bromacil	314–40–9
2-Bromochlorobenzene	694–80–4
3-Bromochlorobenzene	108–39–2
Bromoxynil	1689–84–5
Butachlor	2318–4669
Butylate	2008–41–5
n-C10 (n-decane)	124–18–5
n-C12 (n-undecane)	112–40–2
n-C14 (n-tetradecane)	629–59–4
n-C16 (n-hexadecane)	544–76–3
n-C18 (n-octadecane)	593–45–3
n-C20 (n-eicosane)	112–95–8
n-C22 (n-docosane)	629–97–0
n-C24 (n-tetracosane)	646–31–1
n-C26 (n-hexacosane)	630–01–3
n-C28 (n-octacosane)	630–02–4
n-C30 (n-triacontane)	638–68–6
Captafol	2425–06–1
Captan	133–06–2
Carbaryl	63–25–2
Carbazole	86–74–8
Carbofuran	1563–66–2
Carboxin	5234–68–4
Carbophenothion	786–19–6
Chlordane ^{3,5}	57–74–9
bis(2-Chloroethyl) ether ^{3,4}	111–44–4	5.7	17.1
Chloroneb	2675–77–6
4-Chloroaniline	106–47–8
Chlorobenzilate	510–15–6
Chlorfenvinphos	470–90–6
4-Chloro-2-methylaniline	95–69–2
3-(Chloromethyl)pyridine hydrochloride	6959–48–4
4-Chloro-2-nitroaniline	89–63–4
Chlorpropham	101–21–3
Chlorothalonil	1897–45–6
1-Chloronaphthalene	90–13–1
3-Chloronitrobenzene	121–73–3
4-Chloro-1,2-phenylenediamine	95–83–0

TABLE 3—ADDITIONAL EXTRACTABLE ANALYTES ^{1, 2}—Continued

Analyte	CAS registry	MDL ⁷ (ug/L)	ML ⁸ (ug/L)
4-Chloro-1,3-phenylenediamine	5131-60-2
2-Chlorobiphenyl	2051-60-7
Chlorpyrifos	2921-88-2
Coumaphos	56-72-4
<i>m</i> + <i>p</i> -Cresol	65794-96-9
<i>o</i> -Cresol	95-48-7
<i>p</i> -Cresidine	120-71-8
Crotoxyphos	7700-17-6
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5
Cyanazine	21725-46-2
Cycloate	1134-23-2
<i>p</i> -Cymene	99-87-6
Dacthal (DCPA)	1861-32-1
4,4'-DDD ³	72-54-8	2.8	8.4
4,4'-DDE ³	72-55-9	5.6	16.8
4,4'-DDT ³	50-29-3	4.7	14.1
Demeton-O	298-03-3
Demeton-S	126-75-0
Diallate (<i>cis</i> or <i>trans</i>)	2303-16-4
2,4-Diaminotoluene	95-80-7
Diazinon	333-41-5
Dibenz(a,j)acridine	224-42-0
Dibenzofuran	132-64-9
Dibenzo(a,e)pyrene	192-65-4
Dibenzothiophene	132-65-0
1,2-Dibromo-3-chloropropane	96-12-8
3,5-Dibromo-4-hydroxybenzonitrile	1689-84-5
2,6-Di- <i>tert</i> -butyl- <i>p</i> -benzoquinone	719-22-2
Dichlone	117-80-6
2,3-Dichloroaniline	608-27-5
2,3-Dichlorobiphenyl	16605-91-7
2,6-Dichloro-4-nitroaniline	99-30-9
2,3-Dichloronitrobenzene	3209-22-1
1,3-Dichloro-2-propanol	96-23-1
2,6-Dichlorophenol	120-83-2
Dichlorvos	62-73-7
Dicrotophos	141-66-2
Dieldrin ³	60-57-1	2.5	7.5
1,2:3,4-Diepoxybutane	1464-53-5
Di(2-ethylhexyl) adipate	103-23-1
Diethylstilbestrol	56-53-1
Diethyl sulfate	64-67-5
Dilantin (5,5-Diphenylhydantoin)	57-41-0
Dimethoate	60-51-5
3,3'-Dimethoxybenzidine	119-90-4
Dimethylaminoazobenzene	60-11-7
7,12-Dimethylbenz(a)anthracene	57-97-6
3,3'-Dimethylbenzidine	119-93-7
N,N-Dimethylformamide	68-12-2
3,6-Dimethylphenathrene	1576-67-6
<i>alpha</i> , <i>alpha</i> -Dimethylphenethylamine	122-09-8
Dimethyl sulfone	67-71-0
1,2-Dinitrobenzene	528-29-0
1,3-Dinitrobenzene	99-65-0
1,4-Dinitrobenzene	100-25-4
Dinocap	39300-45-3
Dinoseb	88-85-7
Diphenylamine	122-39-4
Diphenyl ether	101-84-8
1,2-Diphenylhydrazine	122-66-7
Diphenamid	957-51-7
Diphenyldisulfide	882-33-7
Disulfoton	298-04-4
Disulfoton sulfoxide	2497-07-6
Disulfoton sulfone	2497-06-5
Endosulfan I ^{3,4}	959-98-8
Endosulfan II ^{3,4}	33213-65-9
Endosulfan sulfate ³	1031-07-8	5.6	16.8
Endrin ^{3,4}	72-20-8
Endrin aldehyde ^{3,4}	7421-93-4
Endrin ketone ^{3,4}	53494-70-5

TABLE 3—ADDITIONAL EXTRACTABLE ANALYTES ^{1, 2}—Continued

Analyte	CAS registry	MDL ⁷ (ug/L)	ML ⁸ (ug/L)
EPN	2104-64-5
EPTC	759-94-4
Ethion	563-12-2
Ethoprop	13194-48-4
Ethyl carbamate	51-79-6
Ethyl methanesulfonate	65-50-0
Ethylenethiourea	96-45-7
Etridiazole	2593-15-9
Ethynylestradiol-3-methyl ether	72-33-3
Famphur	52-85-7
Fenamiphos	22224-92-6
Fenarimol	60168-88-9
Fensulfothion	115-90-2
Fenthion	55-38-9
Fluchloralin	33245-39-5
Fluridone	59756-60-4
Heptachlor ³	76-44-8	1.9	5.7
Heptachlor epoxide ³	1024-57-3	2.2	6.6
2,2',3,3',4,4',6-Heptachlorobiphenyl	52663-71-5
2,2',4,4',5',6-Hexachlorobiphenyl	60145-22-4
Hexachlorocyclopentadiene ^{3,4}	77-47-4
Hexachlorophene	70-30-4
Hexachloropropene	1888-71-7
Hexamethylphosphoramide	680-31-9
Hexanoic acid	142-62-1
Hexazinone	51235-04-2
Hydroquinone	123-31-9
Isodrin	465-73-6
2-Isopropyl-naphthalene	2027-17-0
Isosafrole	120-58-1
Kepone	143-50-0
Leptophos	21609-90-5
Longifolene	475-20-7
Malachite green	569-64-2
Malathion	121-75-5
Maleic anhydride	108-31-6
Merphos	150-50-5
Mestranol	72-33-3
Methapyrilene	91-80-5
Methoxychlor	72-43-5
2-Methylbenzothiazole	120-75-2
3-Methylcholanthrene	56-49-5
4,4'-Methylenebis(2-chloroaniline)	101-14-4
4,4'-Methylenebis(N,N-dimethylaniline)	101-61-1
4,5-Methylenepheneanthrene	203-64-5
1-Methylfluorene	1730-37-6
Methyl methanesulfonate	66-27-3
2-Methylnaphthalene	91-57-6
Methylparaoxon	950-35-6
Methyl parathion	298-00-0
1-Methylphenanthrene	832-69-9
2-(Methylthio)benzothiazole	615-22-5
Metolachlor	5218-45-2
Metribuzin	21087-64-9
Mevinphos	7786-34-7
Mexacarbate	315-18-4
MGK 264	113-48-4
Mirex	2385-85-5
Molinate	2212-67-1
Monocrotophos	6923-22-4
Naled	300-76-5
Napropamide	15299-99-7
1,4-Naphthoquinone	130-15-4
1-Naphthylamine	134-32-7
2-Naphthylamine	91-59-8
1,5-Naphthalenediamine	2243-62-1
Nicotine	54-11-5
5-Nitroacenaphthene	602-87-9
2-Nitroaniline	88-74-4
3-Nitroaniline	99-09-2
4-Nitroaniline	100-01-6

TABLE 3—ADDITIONAL EXTRACTABLE ANALYTES ^{1, 2}—Continued

Analyte	CAS registry	MDL ⁷ (ug/L)	ML ⁸ (ug/L)
5-Nitro- <i>o</i> -anisidine	99-59-2
4-Nitrobiphenyl	92-93-3
Nitrofen	1836-75-5
5-Nitro- <i>o</i> -toluidine	99-55-8
Nitroquinoline-1-oxide	56-57-5
N-Nitrosodi- <i>n</i> -butylamine ⁴	924-16-3
N-Nitrosodiethylamine ⁴	55-18-5
N-Nitrosodimethylamine ^{3,4}	62-75-9
N-Nitrosodiphenylamine ^{3,4}	86-30-6
N-Nitrosomethylethylamine ⁴	10595-95-6
N-Nitrosomethylphenylamine ⁴	614-00-6
N-Nitrosomorpholine ⁴	59-89-2
N-Nitrosopiperidine ⁴	100-75-5
N-Nitrosopyrrolidine ⁴	930-55-2
<i>trans</i> -Nonachlor	39765-80-5
Norflurazon	27314-13-2
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	40186-71-8
Octamethyl pyrophosphoramidate	152-16-9
4,4'-Oxydianiline	101-80-4
Parathion	56-38-2
PCB-1016 ^{3,5}	12674-11-2
PCB-1221 ^{3,5}	11104-28-2	30	90
PCB-1232 ^{3,5}	11141-16-5
PCB-1242 ^{3,5}	53469-21-9
PCB-1248 ^{3,5}	12672-29-6
PCB-1254 ^{3,5}	11097-69-1	36	108
PCB-1260 ^{3,5}	11098-82-5
PCB-1268 ^{3,5}	11100-14-4
Pebulate	1114-71-2
Pentachlorobenzene	608-93-5
Pentachloronitrobenzene	82-68-8
2,2',3,4',6-Pentachlorobiphenyl	68194-05-8
Pentachloroethane	76-01-7
Pentamethylbenzene	700-12-9
Perylene	198-55-0
Phenacetin	62-44-2
<i>cis</i> -Permethrin	61949-76-6
<i>trans</i> -Permethrin	61949-77-7
Phenobarbital	50-06-6
Phenothiazene	92-84-2
1,4-Phenylenediamine	624-18-0
1-Phenylnaphthalene	605-02-7
2-Phenylnaphthalene	612-94-2
Phorate	298-02-2
Phosalone	2310-18-0
Phosmet	732-11-6
Phosphamidon	13171-21-6
Phthalic anhydride	85-44-9
<i>alpha</i> -Picoline (2-Methylpyridine)	109-06-8
Piperonyl sulfoxide	120-62-7
Prometon	1610-18-0
Prometryn	7287-19-6
Pronamide	23950-58-5
Propachlor	1918-16-7
Propazine	139-40-2
Propylthiouracil	51-52-5
Pyridine	110-86-1
Resorcinol (1,3-Benzenediol)	108-46-3
Safrole	94-59-7
Simazine	122-34-9
Simetryn	1014-70-6
Squalene	7683-64-9
Stirofos	22248-79-9
Strychnine	57-24-9
Styrene ⁹	100-42-5
Sulfallate	95-06-7
Tebuthiuron	34014-18-1
Terbacil	5902-51-2
Terbufos	13071-79-9
Terbutryn	886-50-0
<i>alpha</i> -Terpineol	98-55-5

TABLE 3—ADDITIONAL EXTRACTABLE ANALYTES ^{1, 2}—Continued

Analyte	CAS registry	MDL ⁷ (ug/L)	ML ⁸ (ug/L)
1,2,4,5-Tetrachlorobenzene	95–94–3
2,2',4,4'-Tetrachlorobiphenyl	2437–79–8
2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin	1746–01–6
2,3,4,6-Tetrachlorophenol	58–90–2
Tetrachlorvinphos	22248–79–9
Tetraethyl dithiopyrophosphate	3689–24–5
Tetraethyl pyrophosphate	107–49–3
Thianaphthene (2,3-Benzothiophene)	95–15–8
Thioacetamide	62–55–5
Thionazin	297–97–2
Thiophenol (Benzenethiol)	108–98–5
Thioxanthone	492–22–8
Toluene-1,3-diisocyanate	26471–62–5
Toluene-2,4-diisocyanate	584–84–9
<i>o</i> -Toluidine	95–53–4
Toxaphene ^{3,5}	8001–35–2
Triadimefon	43121–43–3
1,2,3-Trichlorobenzene	87–61–6
2,4,5-Trichlorobiphenyl	15862–07–4
2,3,6-Trichlorophenol	933–75–5
2,4,5-Trichlorophenol	95–95–4
Tricyclazole	41814–78–2
Trifluralin	1582–09–8
1,2,3-Trimethoxybenzene	634–36–6
2,4,5-Trimethylaniline	137–17–7
Trimethyl phosphate	512–56–1
Triphenylene	217–59–4
Tripropyleneglycolmethyl ether	20324–33–8
1,3,5-Trinitrobenzene	99–35–4
Tris(2,3-dibromopropyl) phosphate	126–72–7
Tri- <i>p</i> -tolyl phosphate	78–32–0
O,O,O-Triethyl phosphorothioate	126–68–1
Trithiane	291–29–4
Vernolate	1929–77–7

¹ Compounds that have been demonstrated amenable to extraction and gas chromatography.

² Determine each analyte in the fraction that gives the most accurate result.

³ Priority Pollutant (40 CFR part 423, appendix A).

⁴ See section 1.2.

⁵ These compounds are mixtures of various isomers.

⁶ Detected as azobenzene.

⁷ MDL values from the 1984 promulgated version of Method 625.

⁸ ML = Minimum Level—see Glossary for definition and derivation.

⁹ Styrene may be susceptible to losses during sampling, preservation, and/or extraction of full-volume (1 L) water samples. However, styrene is not regulated at 40 CFR part 136, and it is also listed as an analyte in EPA Method 624.1 and EPA Method 1625C, where such losses may be less than using Method 625.1.

TABLE 4—CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC *m/z*'s FOR BASE/NEUTRAL EXTRACTABLES

Analyte	Retention time (sec) ¹	Characteristic <i>m/z</i> 's					
		Electron impact ionization			Chemical ionization		
		Primary	Second	Second	Methane	Methane	Methane
N-Nitrosodimethylamine	385	42	74	44
bis(2-Chloroethyl) ether	704	93	63	95	63	107	109
bis(2-Chloroisopropyl) ether	799	45	77	79	77	135	137
Hexachloroethane	823	117	201	199	199	201	203
N-Nitrosodi- <i>n</i> -propylamine	830	130	42	101
Nitrobenzene	849	77	123	65	124	152	164
Isophorone	889	82	95	138	139	167	178
bis(2-Chloroethoxy) methane	939	93	95	123	65	107	137
1,2,4-Trichlorobenzene	958	180	182	145	181	183	209
Naphthalene	967	128	129	127	129	157	169
Hexachlorobutadiene	1006	225	223	227	223	225	227
Hexachlorocyclopentadiene	1142	237	235	272	235	237	239
2-Chloronaphthalene	1200	162	164	127	163	191	203
Acenaphthylene	1247	152	151	153	152	153	181
Dimethyl phthalate	1273	163	194	164	151	163	164
2,6-Dinitrotoluene	1300	165	89	121	183	211	223
Acenaphthene	1304	154	153	152	154	155	183
2,4-Dinitrotoluene	1364	165	63	182	183	211	223

TABLE 4—CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC m/z's FOR BASE/NEUTRAL EXTRACTABLES—Continued

Analyte	Retention time (sec) ¹	Characteristic m/z's					
		Electron impact ionization			Chemical ionization		
		Primary	Second	Second	Methane	Methane	Methane
Fluorene	1401	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	1409	204	206	141
Diethyl phthalate	1414	149	177	150	177	223	251
N-Nitrosodiphenylamine	1464	169	168	167	169	170	198
4-Bromophenyl phenyl ether	1498	248	250	141	249	251	277
<i>alpha</i> -BHC	1514	183	181	109
Hexachlorobenzene	1522	284	142	249	284	286	288
<i>beta</i> -BHC	1544	183	181	109
<i>gamma</i> -BHC	1557	181	183	109
Phenanthrene	1583	178	179	176	178	179	207
Anthracene	1592	178	179	176	178	179	207
<i>delta</i> -BHC	1599	183	109	181
Heptachlor	1683	100	272	274
Di- <i>n</i> -butyl phthalate	1723	149	150	104	149	205	279
Aldrin	1753	66	263	220
Fluoranthene	1817	202	101	100	203	231	243
Heptachlor epoxide	1820	353	355	351
<i>gamma</i> -Chlordane	1834	373	375	377
Pyrene	1852	202	101	100	203	231	243
Benzidine ²	1853	184	92	185	185	213	225
<i>alpha</i> -Chlordane	1854	373	375	377
Endosulfan I	1855	237	339	341
4,4'-DDE	1892	246	248	176
Dieldrin	1907	79	263	279
Endrin	1935	81	263	82
Endosulfan II	2014	237	339	341
4,4'-DDD	2019	235	237	165
Endrin aldehyde	2031	67	345	250
Butyl benzyl phthalate	2060	149	91	206	149	299	327
Endosulfan sulfate	2068	272	387	422
4,4'-DDT	2073	235	237	165
Chrysene	2083	228	226	229	228	229	257
3,3'-Dichlorobenzidine	2086	252	254	126
Benzo(a)anthracene	2090	228	229	226	228	229	257
bis(2-Ethylhexyl) phthalate	2124	149	167	279	149
Di- <i>n</i> -octyl phthalate	2240	149	43	57
Benzo(b)fluoranthene	2286	252	253	125	252	253	281
Benzo(k)fluoranthene	2293	252	253	125	252	253	281
Benzo(a)pyrene	2350	252	253	125	252	253	281
Indeno(1,2,3-cd) pyrene	2650	276	138	277	276	277	305
Dibenz(a,h)anthracene	2660	278	139	279	278	279	307
Benzo(ghi)perylene	2750	276	138	277	276	277	305
Toxaphene	159	231	233
PCB 1016	224	260	294
PCB 1221	190	224	260
PCB 1232	190	224	260
PCB 1242	224	260	294
PCB 1248	294	330	262
PCB 1254	294	330	362
PCB 1260	330	362	394

¹ Column: 30 m x 0.25 mm ID; 94% methyl, 5% phenyl, 1% vinyl bonded phase fused silica capillary.

Conditions: 5 min at 30 °C; 30–280 at 8 °C per min; isothermal at 280 °C until benzo(ghi)perylene elutes.

Gas velocity: 30 cm/sec at 30 °C (at constant pressure).

² See section 1.2; included for tailing factor testing.

TABLE 5—CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC m/z's FOR ACID EXTRACTABLES

Analyte	Retention Time (sec) ¹	Characteristic m/z's					
		Electron impact ionization			Chemical ionization		
		Prime	Second	Second	Methane	Methane	Methane
2-Chlorophenol	705	128	64	130	129	131	157
Phenol	700	94	65	66	95	123	135
2-Nitrophenol	900	139	65	109	140	168	122
2,4-Dimethylphenol	924	122	107	121	123	151	163
2,4-Dichlorophenol	947	162	164	98	163	165	167

TABLE 5—CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC m/z's FOR ACID EXTRACTABLES—Continued

Analyte	Retention Time (sec) ¹	Characteristic m/z's					
		Electron impact ionization			Chemical ionization		
		Prime	Second	Second	Methane	Methane	Methane
4-Chloro-3-methylphenol	1091	142	107	144	143	171	183
2,4,6-Trichlorophenol	1165	196	198	200	197	199	201
2,4-Dinitrophenol	1325	184	63	154	185	213	225
4-Nitrophenol	1354	65	139	109	140	168	122
2-Methyl-4,6-dinitrophenol	1435	198	182	77	199	227	239
Pentachlorophenol	1561	266	264	268	267	265	269

Column: 30 m x 0.25 mm ID; 94% methyl, 5% phenyl, 1% vinyl bonded phase fused silica capillary.

Conditions: 5 min at 30 °C; 30–250 at 8 °C per min; isothermal at 280 °C until pentachlorophenol elutes.

Gas velocity: 30 cm/sec at 30 °C (at constant pressure).

TABLE 6—QC ACCEPTANCE CRITERIA—METHOD 625 ¹

Analyte	Range for Q (%) ²	Limit for s (%) ³	Range for X (%) ³	Range for P ₁ , P ₂ (%) ³	Limit for RPD (%)
Acenaphthene	70–130	29	60–132	47–145	48
Acenaphthylene	60–130	45	54–126	33–145	74
Aldrin	7–152	39	7–152	D–166	81
Anthracene	58–130	40	43–120	27–133	66
Benzo(a)anthracene	42–133	32	42–133	33–143	53
Benzo(b)fluoranthene	42–140	43	42–140	24–159	71
Benzo(k)fluoranthene	25–146	38	25–146	11–162	63
Benzo(a)pyrene	32–148	43	32–148	17–163	72
Benzo(ghi)perylene	13–195	61	D–195	D–219	97
Benzyl butyl phthalate	43–140	36	D–140	D–152	60
beta-BHC	42–131	37	42–131	24–149	61
delta-BHC	D–130	77	D–120	D–120	129
bis(2-Chloroethyl)ether	52–130	65	43–126	12–158	108
bis(2-Chloroethoxy)methane	52–164	32	49–165	33–184	54
bis(2-Chloroisopropyl) ether	63–139	46	63–139	36–166	76
bis(2-Ethylhexyl) phthalate	43–137	50	29–137	8–158	82
4-Bromophenyl phenyl ether	70–130	26	65–120	53–127	43
2-Chloronaphthalene	70–130	15	65–120	60–120	24
4-Chlorophenyl phenyl ether	57–145	36	38–145	25–158	61
Chrysene	44–140	53	44–140	17–168	87
4,4'-DDD	D–135	56	D–135	D–145	93
4,4'-DDE	19–130	46	19–120	4–136	77
4,4'-DDT	D–171	81	D–171	D–203	135
Dibenz(a,h)anthracene	13–200	75	D–200	D–227	126
Di-n-butyl phthalate	52–130	28	8–120	1–120	47
3,3'-Dichlorobenzidine	18–213	65	8–213	D–262	108
Dieldrin	70–130	38	44–119	29–136	62
Diethyl phthalate	47–130	60	D–120	D–120	100
Dimethyl phthalate	50–130	110	D–120	D–120	183
2,4-Dinitrotoluene	53–130	25	48–127	39–139	42
2,6-Dinitrotoluene	68–137	29	68–137	50–158	48
Di-n-octyl phthalate	21–132	42	19–132	4–146	69
Endosulfan sulfate	D–130	42	D–120	D–120	70
Endrin aldehyde	D–189	45	D–189	D–209	75
Fluoranthene	47–130	40	43–121	26–137	66
Fluorene	70–130	23	70–120	59–121	38
Heptachlor	D–172	44	D–172	D–192	74
Heptachlor epoxide	70–130	61	71–120	26–155	101
Hexachlorobenzene	38–142	33	8–142	D–152	55
Hexachlorobutadiene	68–130	38	38–120	24–120	62
Hexachloroethane	55–130	32	55–120	40–120	52
Indeno(1,2,3-cd)pyrene	13–151	60	D–151	D–171	99
Isophorone	52–180	56	47–180	21–196	93
Naphthalene	70–130	39	36–120	21–133	65
Nitrobenzene	54–158	37	54–158	35–180	62
N-Nitrosodi-n-propylamine	59–170	52	14–198	D–230	87
PCB–1260	19–130	77	19–130	D–164	128
Phenanthrene	67–130	24	65–120	54–120	39
Pyrene	70–130	30	70–120	52–120	49
1,2,4-Trichlorobenzene	61–130	30	57–130	44–142	50
4-Chloro-3-methylphenol	68–130	44	41–128	22–147	73
2-Chlorophenol	55–130	37	36–120	23–134	61
2,4-Dichlorophenol	64–130	30	53–122	39–135	50

TABLE 6—QC ACCEPTANCE CRITERIA—METHOD 625 ¹—Continued

Analyte	Range for Q (%) ²	Limit for s (%) ³	Range for \bar{X} (%) ³	Range for P ₁ , P ₂ (%) ³	Limit for RPD (%)
2,4-Dimethylphenol	58–130	35	42–120	32–120	58
2,4-Dinitrophenol	39–173	79	D–173	D–191	132
2-Methyl-4,6-dinitrophenol	56–130	122	53–130	D–181	203
2-Nitrophenol	61–163	33	45–167	29–182	55
4-Nitrophenol	35–130	79	13–129	D–132	131
Pentachlorophenol	42–152	52	38–152	14–176	86
Phenol	48–130	39	17–120	5–120	64
2,4,6-Trichlorophenol	69–130	35	52–129	37–144	58

¹ Acceptance criteria are based upon method performance data in Table 7 and from EPA Method 1625. Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those used to develop Table 7.

² Test concentration = 100 µg/mL.

³ Test concentration = 100 µg/L.

Q = Calibration verification (sections 7.3.1 and 13.4).

s = Standard deviation for four recovery measurements in the DOC test (section 8.2.4).

\bar{X} = Average recovery for four recovery measurements in the DOC test (section 8.2.4).

P₁, P₂ = MS/MSD recovery (section 8.3.2, section 8.4.2).

RPD = MS/MSD relative percent difference (RPD; section 8.3.3).

D = Detected; result must be greater than zero.

TABLE 7—PRECISION AND RECOVERY AS FUNCTIONS OF CONCENTRATION—METHOD 625 ¹

Analyte	Recovery, \bar{X} (µg/L)	Single analyst precision, s_r (µg/L)	Overall precision, S' (µg/L)
Acenaphthene	0.96C + 0.19	0.15 \bar{X} – 0.12	0.21 \bar{X} – 0.67
Acenaphthylene	0.89C + 0.74	0.24 \bar{X} – 1.06	0.26 \bar{X} – 0.54
Aldrin	0.78C + 1.66	0.27 \bar{X} – 1.28	0.43 \bar{X} + 1.13
Anthracene	0.80C + 0.68	0.21 \bar{X} – 0.32	0.27 \bar{X} – 0.64
Benzo(a)anthracene	0.88C – 0.60	0.15 \bar{X} + 0.93	0.26 \bar{X} – 0.28
Benzo(b)fluoranthene	0.93C – 1.80	0.22 \bar{X} + 0.43	0.29 \bar{X} + 0.96
Benzo(k)fluoranthene	0.87C – 1.56	0.19 \bar{X} + 1.03	0.35 \bar{X} + 0.40
Benzo(a)pyrene	0.90C – 0.13	0.22 \bar{X} + 0.48	0.32 \bar{X} + 1.35
Benzo(ghi)perylene	0.98C – 0.86	0.29 \bar{X} + 2.40	0.51 \bar{X} – 0.44
Benzyl butyl phthalate	0.66C – 1.68	0.18 \bar{X} + 0.94	0.53 \bar{X} + 0.92
beta-BHC	0.87C – 0.94	0.20 \bar{X} – 0.58	0.30 \bar{X} – 1.94
delta-BHC	0.29C – 1.09	0.34 \bar{X} + 0.86	0.93 \bar{X} – 0.17
bis(2-Chloroethyl) ether	0.86C – 1.54	0.35 \bar{X} – 0.99	0.35 \bar{X} + 0.10
bis(2-Chloroethoxy) methane	1.12C – 5.04	0.16 \bar{X} + 1.34	0.26 \bar{X} + 2.01
bis(2-Chloroisopropyl) ether	1.03C – 2.31	0.24 \bar{X} + 0.28	0.25 \bar{X} + 1.04
bis(2-Ethylhexyl) phthalate	0.84C – 1.18	0.26 \bar{X} + 0.73	0.36 \bar{X} + 0.67
4-Bromophenyl phenyl ether	0.91C – 1.34	0.13 \bar{X} + 0.66	0.16 \bar{X} + 0.66
2-Chloronaphthalene	0.89C + 0.01	0.07 \bar{X} + 0.52	0.13 \bar{X} + 0.34
4-Chlorophenyl phenyl ether	0.91C + 0.53	0.20 \bar{X} – 0.94	0.30 \bar{X} – 0.46
Chrysene	0.93C – 1.00	0.28 \bar{X} + 0.13	0.33 \bar{X} – 0.09
4,4'-DDD	0.56C – 0.40	0.29 \bar{X} – 0.32	0.66 \bar{X} – 0.96
4,4'-DDE	0.70C – 0.54	0.26 \bar{X} – 1.17	0.39 \bar{X} – 1.04
4,4'-DDT	0.79C – 3.28	0.42 \bar{X} + 0.19	0.65 \bar{X} – 0.58
Dibenz(a,h)anthracene	0.88C + 4.72	0.30 \bar{X} + 8.51	0.59 \bar{X} + 0.25
Di-n-butyl phthalate	0.59C + 0.71	0.13 \bar{X} + 1.16	0.39 \bar{X} + 0.60
3,3'-Dichlorobenzidine	1.23C – 12.65	0.28 \bar{X} + 7.33	0.47 \bar{X} + 3.45
Dieldrin	0.82C – 0.16	0.20 \bar{X} – 0.16	0.26 \bar{X} – 0.07
Diethyl phthalate	0.43C + 1.00	0.28 \bar{X} + 1.44	0.52 \bar{X} + 0.22
Dimethyl phthalate	0.20C + 1.03	0.54 \bar{X} + 0.19	1.05 \bar{X} – 0.92
2,4-Dinitrotoluene	0.92C – 4.81	0.12 \bar{X} + 1.06	0.21 \bar{X} + 1.50
2,6-Dinitrotoluene	1.06C – 3.60	0.14 \bar{X} + 1.26	0.19 \bar{X} + 0.35
Di-n-octyl phthalate	0.76C – 0.79	0.21 \bar{X} + 1.19	0.37 \bar{X} + 1.19
Endosulfan sulfate	0.39C + 0.41	0.12 \bar{X} + 2.47	0.63 \bar{X} – 1.03
Endrin aldehyde	0.76C – 3.86	0.18 \bar{X} + 3.91	0.73 \bar{X} – 0.62
Fluoranthene	0.81C + 1.10	0.22 \bar{X} + 0.73	0.28 \bar{X} – 0.60
Fluorene	0.90C – 0.00	0.12 \bar{X} + 0.26	0.13 \bar{X} + 0.61
Heptachlor	0.87C – 2.97	0.24 \bar{X} – 0.56	0.50 \bar{X} – 0.23
Heptachlor epoxide	0.92C – 1.87	0.33 \bar{X} – 0.46	0.28 \bar{X} + 0.64
Hexachlorobenzene	0.74C + 0.66	0.18 \bar{X} – 0.10	0.43 \bar{X} – 0.52
Hexachlorobutadiene	0.71C – 1.01	0.19 \bar{X} + 0.92	0.26 \bar{X} + 0.49
Hexachloroethane	0.73C – 0.83	0.17 \bar{X} + 0.67	0.17 \bar{X} + 0.80
Indeno(1,2,3-cd)pyrene	0.78C – 3.10	0.29 \bar{X} + 1.46	0.50 \bar{X} + 0.44
Isophorone	1.12C + 1.41	0.27 \bar{X} + 0.77	0.33 \bar{X} + 0.26
Naphthalene	0.76C + 1.58	0.21 \bar{X} – 0.41	0.30 \bar{X} – 0.68
Nitrobenzene	1.09C – 3.05	0.19 \bar{X} + 0.92	0.27 \bar{X} + 0.21
N-Nitrosodi-n-propylamine	1.12C – 6.22	0.27 \bar{X} + 0.68	0.44 \bar{X} + 0.47

TABLE 7—PRECISION AND RECOVERY AS FUNCTIONS OF CONCENTRATION—METHOD 625¹—Continued

Analyte	Recovery, X' ($\mu\text{g/L}$)	Single analyst precision, s_r' ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
PCB-1260	$0.81C - 10.86$	$0.35 \bar{X} + 3.61$	$0.43 \bar{X} + 1.82$
Phenanthrene	$0.87C - 0.06$	$0.12 \bar{X} + 0.57$	$0.15 \bar{X} + 0.25$
Pyrene	$0.84C - 0.16$	$0.16 \bar{X} + 0.06$	$0.15 \bar{X} + 0.31$
1,2,4-Trichlorobenzene	$0.94C - 0.79$	$0.15 \bar{X} + 0.85$	$0.21 \bar{X} + 0.39$
4-Chloro-3-methylphenol	$0.84C + 0.35$	$0.23 \bar{X} + 0.75$	$0.29 \bar{X} + 1.31$
2-Chlorophenol	$0.78C + 0.29$	$0.18 \bar{X} + 1.46$	$0.28 \bar{X} + 0.97$
2,4-Dichlorophenol	$0.87C + 0.13$	$0.15 \bar{X} + 1.25$	$0.21 \bar{X} + 1.28$
2,4-Dimethylphenol	$0.71C + 4.41$	$0.16 \bar{X} + 1.21$	$0.22 \bar{X} + 1.31$
2,4-Dinitrophenol	$0.81C - 18.04$	$0.38 \bar{X} + 2.36$	$0.42 \bar{X} + 26.29$
2-Methyl-4,6-Dinitrophenol	$1.04C - 28.04$	$0.05 \bar{X} + 42.29$	$0.26 \bar{X} + 23.10$
2-Nitrophenol	$1.07C - 1.15$	$0.16 \bar{X} + 1.94$	$0.27 \bar{X} + 2.60$
4-Nitrophenol	$0.61C - 1.22$	$0.38 \bar{X} + 2.57$	$0.44 \bar{X} + 3.24$
Pentachlorophenol	$0.93C + 1.99$	$0.24 \bar{X} + 3.03$	$0.30 \bar{X} + 4.33$
Phenol	$0.43C + 1.26$	$0.26 \bar{X} + 0.73$	$0.35 \bar{X} + 0.58$
2,4,6-Trichlorophenol	$0.91C - 0.18$	$0.16 \bar{X} + 2.22$	$0.22 \bar{X} + 1.81$

¹ Regressions based on data from Reference 2. X' = Expected recovery for one or more measurements of a sample containing a concentration of C , in $\mu\text{g/L}$. s_r' = Expected single analyst standard deviation of measurements at an average concentration found of \bar{X} , in $\mu\text{g/L}$. S' = Expected interlaboratory standard deviation of measurements at an average concentration found of \bar{X} , in $\mu\text{g/L}$. C = True value for the concentration, in $\mu\text{g/L}$. \bar{X} = Average recovery found for measurements of samples containing a concentration of C , in $\mu\text{g/L}$.

TABLE 8—SUGGESTED INTERNAL AND SURROGATE STANDARDS

Base/neutral fraction	Range for surrogate recovery (%) ¹	
	Calibration verification	Recovery from samples
Acenaphthalene- d_8	66–152	33–168
Acenaphthene- d_{10}	71–141	30–180
Aniline- d_5		
Anthracene- d_{10}	58–171	23–142
Benzo(a)anthracene- d_{12}	28–357	22–329
Benzo(a)pyrene- d_{12}	32–194	32–194
4-Chloroaniline- d_4	1–145	1–145
bis(2-Chloroethyl) ether- d_8	52–194	25–222
Chrysene- d_{12}	23–290	23–290
Decafluorobiphenyl		
4,4'-Dibromobiphenyl		
4,4'-Dibromooctafluorobiphenyl		
1,4-Dichlorobenzene- d_4	65–153	11–245
2,2'-Difluorobiphenyl		
Dimethyl phthalate- d_6	47–211	1–500
Fluoranthene- d_{10}	47–215	30–187
Fluorene- d_{10}	61–164	38–172
4-Fluoroaniline		
1-Fluoronaphthalene		
2-Fluoronaphthalene		
2-Methylnaphthalene- d_{10}	50–150	50–150
Naphthalene- d_8	71–141	22–192
Nitrobenzene- d_5	46–219	15–314
2,3,4,5,6-Pentafluorobiphenyl		
Perylene- d_{12}		
Phenanthrene- d_{10}	67–149	34–168
Pyrene- d_{10}	48–210	28–196
Pyridine- d_5		
Acid fraction		
2-Chlorophenol- d_4	55–180	33–180
2,4-Dichlorophenol- d_3	64–157	34–182
4,6-Dinitro-2-methylphenol- d_2	56–177	22–307
2-Fluorophenol		
4-Methylphenol- d_8	25–111	25–111
2-Nitrophenol- d_4	61–163	37–163
4-Nitrophenol- d_4	35–287	6–500
Pentafluorophenol		
2-Perfluoromethylphenol		
Phenol- d_5	48–208	8–424

¹ Recovery from samples is the wider of the criteria in the CLP SOW for organics or in Method 1625.

TABLE 9A—DFTPP KEY m/z's AND ABUNDANCE CRITERIA FOR QUADRUPOLE INSTRUMENTS ¹

m/z	Abundance criteria
51	30–60 percent of m/z 198.
68	Less than 2 percent of m/z 69.
70	Less than 2 percent of m/z 69.
127	40–60 percent of base peak m/z 198.
197	Less than 1 percent of m/z 198.
198	Base peak, 100 percent relative abundance.
199	5–9 percent of m/z 198.
275	10–30 percent of m/z 198.
365	Greater than 1 percent of m/z 198.
441	Present but less than m/z 443.
442	40–100 percent of m/z 198.
443	17–23 percent of m/z 442.

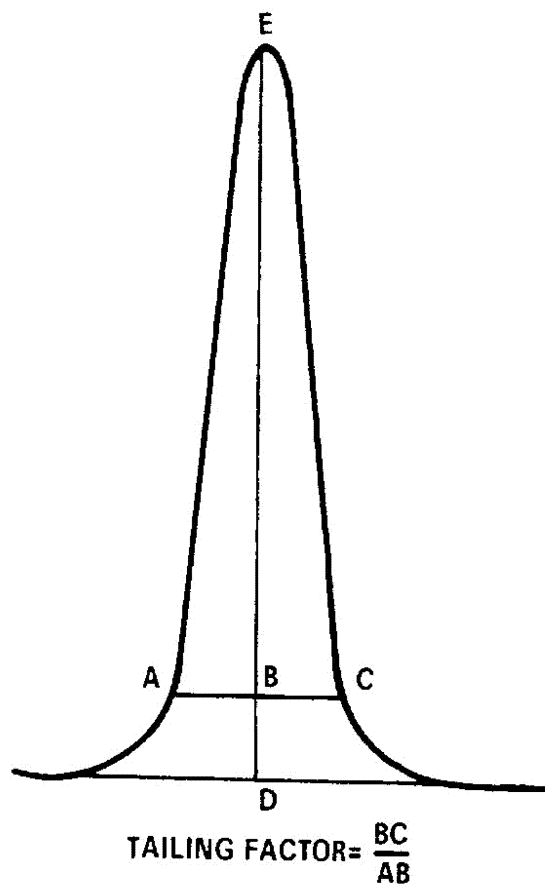
¹ Criteria in these tables are for quadrupole and time-of-flight instruments. Alternative tuning criteria from other published EPA reference methods may be used provided method performance is not adversely affected. Alternative tuning criteria specified by an instrument manufacturer may also be used for another type of mass spectrometer, provided method performance is not adversely affected.

TABLE 9B—DFTPP KEY m/z's AND ABUNDANCE CRITERIA FOR TIME-OF-FLIGHT INSTRUMENTS ¹

m/z	Abundance criteria
51	10–85 percent of the base peak.
68	Less than 2 percent of m/z 69.
70	Less than 2 percent of m/z 69.
127	10–80 percent of the base peak.
197	Less than 2 percent of Mass 198.
198	Base peak, or greater than 50% of m/z 442.
199	5–9 percent of m/z 198.
275	10–60 percent of the base peak.
365	Greater than 0.5 percent of m/z 198.
441	Less than 150 percent of m/z 443.
442	Base peak or greater than 30 percent of m/z 198.
443	15–24 percent of m/z 442.

¹ Criteria in these tables are for quadrupole and time-of-flight instruments. Alternative tuning criteria from other published EPA reference methods may be used provided method performance is not adversely affected. Alternative tuning criteria specified by an instrument manufacturer may also be used for another type of mass spectrometer, or for an alternative carrier gas, provided method performance is not adversely affected.

21. Figures



Example calculation: Peak Height = DE = 100 mm

10% Peak Height = BD = 10 mm

Peak Width at 10% Peak Height = AC = 23 mm

AB = 11 mm

BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11} = 1.1$

Figure 1 Tailing factor calculation

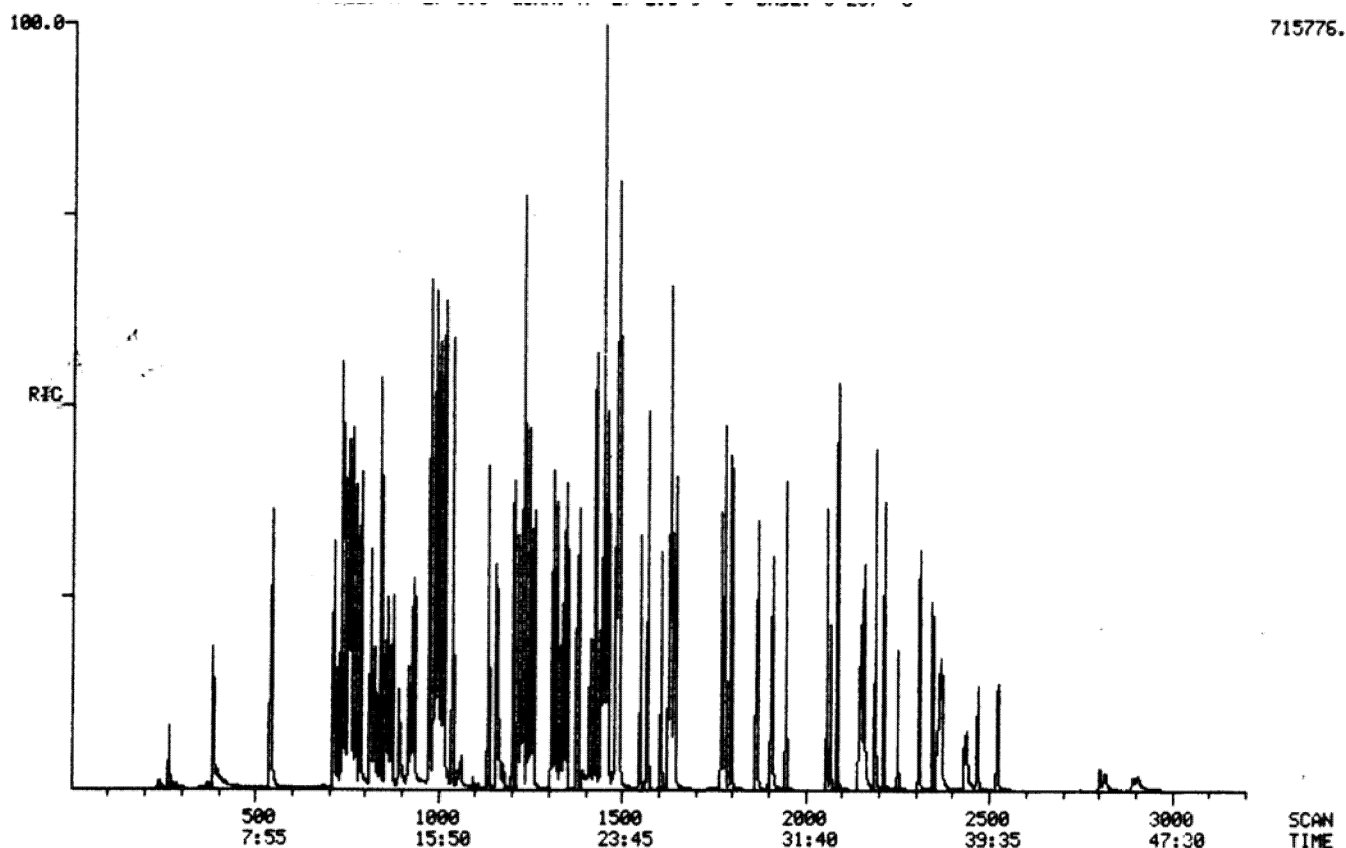


Figure 2 Chromatogram of combined acid/base/neutral standard

22. Glossary

These definitions and purposes are specific to this method but have been conformed to common usage to the extent possible.

22.1 Units of weight and measure and their abbreviations.

22.1.1 Symbols.

°C degrees Celsius

µg microgram

µL microliter

< less than

> greater than

≤ less than or equal to

% percent

22.1.2 Abbreviations (in alphabetical order).

cm centimeter

g gram

h hour

ID inside diameter

in. inch

L liter

m mass or meter

mg milligram

min minute

mL milliliter

mm millimeter

ms millisecond

m/z mass-to-charge ratio

N normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution

ng nanogram

pg picogram

ppb part-per-billion

ppm part-per-million

ppt part-per-trillion

psig pounds-per-square inch gauge

22.2 Definitions and acronyms (in alphabetical order).

Analyte—A compound or mixture of compounds (e.g., PCBs) tested for by this method. The analytes are listed in Tables 1–3.

Batch—See Extraction.

Blank—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Calibration—The process of determining the relationship between the output or response of a measuring instrument and the value of an input standard. Historically, EPA has referred to a multi-point calibration as the “initial calibration,” to differentiate it from a single-point calibration verification.

Calibration standard—A solution prepared from stock solutions and/or a secondary standards and containing the analytes of interest, surrogates, and internal standards. The calibration standard is used to calibrate the response of the GC/MS instrument against analyte concentration.

Calibration verification standard—The mid-point calibration standard used to verify calibration. See sections 7.3 and 13.4.

Descriptor—In SIM, the beginning and ending retention times for the RT window,

the m/z's sampled in the RT window, and the dwell time at each m/z.

Extracted ion current profile (EICP)—The line described by the signal at a given m/z.

Extraction Batch—A set of up to 20 field samples (not including QC samples) started through the extraction process on a given 24-hour shift (section 3.1). Each extraction batch must be accompanied by a blank (section 8.5), a laboratory control sample (LCS, section 8.4), and a matrix spike and duplicate (MS/MSD; Section 8.3), resulting in a minimum of five analyses (1 sample, 1 blank, 1 LCS, 1 MS, and 1 MSD) and a maximum of 24 analyses (20 field samples, 1 blank, 1 LCS, 1 MS, and 1 MSD) for the batch. If greater than 20 samples are to be extracted in a 24-hour shift, the samples must be separated into extraction batches of 20 or fewer samples.

Field Duplicates—Two samples collected at the same time and placed under identical conditions, and treated identically throughout field and laboratory procedures. Results of analyses of the field duplicates provide an estimate of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Field blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to

determine if the field or sample transporting procedures and environments have contaminated the sample.

GC—Gas chromatograph or gas chromatography.

Internal standard—A compound added to an extract or standard solution in a known amount and used as a reference for quantitation of the analytes of interest and surrogates. In this method the internal standards are stable isotopically labeled analogs of selected method analytes (Table 8). Also see Internal standard quantitation.

Internal standard quantitation—A means of determining the concentration of an analyte of interest (Tables 1–3) by reference to a compound not expected to be found in a sample.

DOC—Initial demonstration of capability (section 8.2); four aliquots of reagent water spiked with the analytes of interest and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. A DOC is performed prior to the first time this method is used and any time the method or instrumentation is modified.

Laboratory Control Sample (LCS; laboratory fortified blank; section 8.4)—An aliquot of reagent water spiked with known quantities of the analytes of interest and surrogates. The LCS is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

Laboratory fortified sample matrix—See Matrix spike.

Laboratory reagent blank—A blank run on laboratory reagents; e.g., methylene chloride (section 11.1.5).

Matrix spike (MS) and matrix spike duplicate (MSD) (laboratory fortified sample matrix and duplicate)—Two aliquots of an environmental sample to which known quantities of the analytes of interest and surrogates are added in the laboratory. The MS/MSD are prepared and analyzed exactly like a field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

May—This action, activity, or procedural step is neither required nor prohibited.

May not—This action, activity, or procedural step is prohibited.

Method blank—See blank.

Method detection limit (MDL)—A detection limit determined by the procedure at 40 CFR part 136, appendix B. The MDLs determined by EPA in the original version of the method are listed in Tables 1, 2 and 3. As noted in section 1.5, use the MDLs in Tables 1, 2, and 3 in conjunction with current MDL data from the laboratory actually analyzing samples to assess the sensitivity of this procedure relative to project objectives and regulatory requirements (where applicable).

Minimum level (ML)—The term “minimum level” refers to either the sample concentration equivalent to the lowest

calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher. Minimum levels may be obtained in several ways: They may be published in a method; they may be based on the lowest acceptable calibration point used by a laboratory; or they may be calculated by multiplying the MDL in a method, or the MDL determined by a laboratory, by a factor of 3. For the purposes of NPDES compliance monitoring, EPA considers the following terms to be synonymous: “quantitation limit,” “reporting limit,” and “minimum level.”

MS—Mass spectrometer or mass spectrometry, or matrix spike (a QC sample type).

MSD—Matrix spike duplicate (a QC sample type).

Must—This action, activity, or procedural step is required.

m/z—The ratio of the mass of an ion (m) detected in the mass spectrometer to the charge (z) of that ion.

Preparation blank—See blank.

Quality control check sample (QCS)—See Laboratory Control Sample.

Reagent water—Water demonstrated to be free from the analytes of interest and potentially interfering substances at the MDLs for the analytes in this method.

Regulatory compliance limit (or regulatory concentration limit)—A limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory/control authority.

Relative retention time (RRT)—The ratio of the retention time of an analyte to the retention time of its associated internal standard. RRT compensates for small changes in the GC temperature program that can affect the absolute retention times of the analyte and internal standard. RRT is a unitless quantity.

Relative standard deviation (RSD)—The standard deviation times 100 divided by the mean. Also termed “coefficient of variation.”

RF—Response factor. See section 7.2.2.

RSD—See relative standard deviation.

Safety Data Sheet (SDS)—Written information on a chemical's toxicity, health hazards, physical properties, fire, and reactivity, including storage, spill, and handling precautions that meet the requirements of OSHA, 29 CFR 1910.1200(g) and appendix D to § 1910.1200. United Nations Globally Harmonized System of Classification and Labelling of Chemicals (GHS), third revised edition, United Nations, 2009.

Selected Ion Monitoring (SIM)—An MS technique in which a few m/z's are monitored. When used with gas chromatography, the m/z's monitored are usually changed periodically throughout the chromatographic run, to correlate with the characteristic m/z's of the analytes, surrogates, and internal standards as they elute from the chromatographic column. The technique is often used to increase sensitivity and minimize interferences.

Signal-to-noise ratio (S/N)—The height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the width of the noise.

Should—This action, activity, or procedural step is suggested but not required.

SPE—Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous solution by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

Stock solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity, authenticity, and concentration of the standard.

Surrogate—A compound unlikely to be found in a sample, and which is spiked into sample in a known amount before extraction or other processing, and is quantitated with the same procedures used to quantify other sample components. The purpose of the surrogate is to monitor method performance with each sample.

* * * * *

■ 9. Appendix B to part 136 is revised to read as follows:

Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 2

Definition

The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

I. Scope and Application

(1) The MDL procedure is designed to be a straightforward technique for estimation of the detection limit for a broad variety of physical and chemical methods. The procedure requires a complete, specific, and well-defined analytical method. It is essential that all sample processing steps used by the laboratory be included in the determination of the method detection limit.

(2) The MDL procedure is *not* applicable to methods that do not produce results with a continuous distribution, such as, but not limited to, methods for whole effluent toxicity, presence/absence methods, and microbiological methods that involve counting colonies. The MDL procedure also is *not* applicable to measurements such as, but not limited to, biochemical oxygen demand, color, pH, specific conductance, many titration methods, and any method where low-level spiked samples cannot be prepared. Except as described in the addendum, for the purposes of this procedure, “spiked samples” are prepared from a clean reference matrix, such as reagent water, spiked with a known and consistent quantity of the analyte. MDL determinations using spiked samples may not be appropriate for all gravimetric methods (e.g., residue or total suspended solids), but an MDL based on method blanks can be determined in such instances.

II. Procedure

(1) Estimate the initial MDL using one or more of the following:

(a) The mean determined concentration plus three times the standard deviation of a set of method blanks.

(b) The concentration value that corresponds to an instrument signal-to-noise ratio in the range of 3 to 5.

(c) The concentration equivalent to three times the standard deviation of replicate instrumental measurements of spiked blanks.

(d) That region of the calibration where there is a significant change in sensitivity, *i.e.*, a break in the slope of the calibration.

(e) Instrumental limitations.

(f) Previously determined MDL.

Note: It is recognized that the experience of the analyst is important to this process. However, the analyst should include some or all of the above considerations in the initial estimate of the MDL.

(2) Determine the initial MDL.

Note: The Initial MDL is used when the laboratory does not have adequate data to perform the Ongoing Annual Verification specified in Section (4), typically when a new method is implemented or if a method was rarely used in the last 24 months.

(a) Select a spiking level, typically 2—10 times the estimated MDL in Section 1. Spiking levels in excess of 10 times the estimated detection limit may be required for analytes with very poor recovery (*e.g.*, for an analyte with 10% recovery, spiked at 100 micrograms/L, with mean recovery of 10 micrograms/L; the calculated MDL may be around 3 micrograms/L. Therefore, in this example, the spiking level would be 33 times the MDL, but spiking lower may result in no recovery at all).

(b) Process a minimum of seven spiked samples and seven method blank samples through all steps of the method. The samples used for the MDL must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates. (Preparation and analysis may be on the same day.) Existing data may be used, if compliant with the requirements for at least three batches, and generated within the last twenty four months. The most recent available data for method blanks and spiked samples must be used. Statistical outlier removal procedures should not be used to remove data for the initial MDL determination, since the total number of observations is small and the purpose of the MDL procedure is to capture routine method variability. However, documented instances of gross failures (*e.g.*, instrument malfunctions, mislabeled samples, cracked vials) may be excluded from the calculations, provided that at least seven spiked samples and seven method blanks are available. (The rationale for removal of specific outliers must be documented and maintained on file with the results of the MDL determination.)

(i) If there are multiple instruments that will be assigned the same MDL, then the sample analyses must be distributed across all of the instruments.

(ii) A minimum of two spiked samples and two method blank samples prepared and analyzed on different calendar dates is required for each instrument. Each analytical batch may contain one spiked sample and one method blank sample run together. A

spiked sample and a method blank sample may be analyzed in the same batch, but are not required to be.

(iii) The same prepared extract may be analyzed on multiple instruments so long as the minimum requirement of seven preparations in at least three separate batches is maintained.

(c) Evaluate the spiking level: If any result for any individual analyte from the spiked samples does not meet the method qualitative identification criteria or does not provide a numerical result greater than zero, then repeat the spiked samples at a higher concentration. (Qualitative identification criteria are a set of rules or guidelines for establishing the identification or presence of an analyte using a measurement system. Qualitative identification does not ensure that quantitative results for the analyte can be obtained.)

(d) Make all computations as specified in the analytical method and express the final results in the method-specified reporting units.

(i) Calculate the sample standard deviation (S) of the replicate spiked sample measurements and the sample standard deviation of the replicate method blank measurements from all instruments to which the MDL will be applied.

(ii) Compute the MDL_s (the MDL based on spiked samples) as follows:

$$MDL_s = t_{(n-1, 1-\alpha=0.99)} S_s$$

Where:

MDL_s = the method detection limit based on spiked samples

$t_{(n-1, 1-\alpha=0.99)}$ = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with $n-1$ degrees of freedom. See Addendum Table 1.

S_s = sample standard deviation of the replicate spiked sample analyses.

(iii) Compute the MDL_b (the MDL based on method blanks) as follows:

(A) If none of the method blanks give numerical results for an individual analyte, the MDL_b does not apply. A numerical result includes both positive and negative results, including results below the current MDL, but not results of "ND" (not detected) commonly observed when a peak is not present in chromatographic analysis.

(B) If some (but not all) of the method blanks for an individual analyte give numerical results, set the MDL_b equal to the highest method blank result. If more than 100 method blanks are available, set MDL_b to the level that is no less than the 99th percentile of the method blank results. For "n" method blanks where $n \geq 100$, sort the method blanks in rank order. The $(n * 0.99)$ ranked method blank result (round to the nearest whole number) is the MDL_b . For example, to find MDL_b from a set of 164 method blanks where the highest ranked method blank results are . . . 1.5, 1.7, 1.9, 5.0, and 10, then $164 * 0.99 = 162.36$ which rounds to the 162nd method blank result. Therefore, MDL_b is 1.9 for $n = 164$ (10 is the 164th result, 5.0 is the 163rd result, and 1.9 is the 162nd result).

Alternatively, you may use spreadsheet algorithms to calculate the 99th percentile to interpolate between the ranks more precisely.

(C) If all of the method blanks for an individual analyte give numerical results, then calculate the MDL_b as:

$$MDL_b = \bar{X} + t_{(n-1, 1-\alpha=0.99)} S_b$$

Where:

MDL_b = the MDL based on method blanks
 \bar{X} = mean of the method blank results (use zero in place of the mean if the mean is negative)

$t_{(n-1, 1-\alpha=0.99)}$ = the Student's t-value appropriate for the single-tailed 99th percentile t statistic and a standard deviation estimate with $n-1$ degrees of freedom. See Addendum Table 1.

S_b = sample standard deviation of the replicate method blank sample analyses.

Note: If 100 or more method blanks are available, as an option, MDL_b may be set to the concentration that is greater than or equal to the 99th percentile of the method blank results, as described in Section (2)(d)(iii)(B).

(e) Select the greater of MDL_s or MDL_b as the initial MDL.

(3) Ongoing Data Collection.

(a) During any quarter in which samples are being analyzed, prepare and analyze a minimum of two spiked samples on each instrument, in separate batches, using the same spiking concentration used in Section 2. If any analytes are repeatedly not detected in the quarterly spiked sample analyses, or do not meet the qualitative identification criteria of the method (see section 2(c) of this procedure), then this is an indication that the spiking level is not high enough and should be adjusted upward. Note that it is not necessary to analyze additional method blanks together with the spiked samples, the method blank population should include all of the routine method blanks analyzed with each batch during the course of sample analysis.

(b) Ensure that at least seven spiked samples and seven method blanks are completed for the annual verification. If only one instrument is in use, a minimum of seven spikes are still required, but they may be drawn from the last two years of data collection.

(c) At least once per year, re-evaluate the spiking level.

(i) If more than 5% of the spiked samples do not return positive numerical results that meet all method qualitative identification criteria, then the spiking level must be increased and the initial MDL re-determined following the procedure in section 2.

(ii) [Reserved]

(d) If the method is altered in a way that can be reasonably expected to change its sensitivity, then re-determine the initial MDL according to section 2, and the restart the ongoing data collection.

(e) If a new instrument is added to a group of instruments whose data are being pooled to create a single MDL, analyze a minimum of two spiked replicates and two method blank replicates on the new instrument. If both method blank results are below the existing MDL, then the existing MDL_b is validated. Combine the new spiked sample results to the existing spiked sample results and recalculate the MDL_s as in Section 4. If the recalculated MDL_s does not vary by more than the factor specified in section 4(f) of this

procedure, then the existing MDL_s is validated. If either of these two conditions is not met, then calculate a new MDL following the instructions in section 2.

(4) Ongoing Annual Verification.

(a) At least once every thirteen months, recalculate MDL_s and MDL_b from the collected spiked samples and method blank results using the equations in section 2.

(b) Include data generated within the last twenty four months, but only data with the same spiking level. Only documented instances of gross failures (e.g., instrument malfunctions, mislabeled samples, cracked vials) may be excluded from the calculations. (The rationale for removal of specific outliers must be documented and maintained on file with the results of the MDL determination.) If the laboratory believes the sensitivity of the method has changed significantly, then the most recent data available may be used, maintaining compliance with the requirement for at least seven replicates in three separate batches on three separate days (see section 2b).

(c) Include the initial MDL spiked samples, if the data were generated within twenty four months.

(d) Only use data associated with acceptable calibrations and batch QC. Include all routine data, with the exception of batches that are rejected and the associated samples reanalyzed. If the method has been altered in a way that can be reasonably expected to change its sensitivity, then use only data collected after the change.

(e) Ideally, use all method blank results from the last 24 months for the MDL_b calculation. The laboratory has the option to use only the last six months of method blank data or the fifty most recent method blanks, whichever criteria yields the greater number of method blanks.

(f) The verified MDL is the greater of the MDL_s or MDL_b. If the verified MDL is within 0.5 to 2.0 times the existing MDL, and fewer than 3% of the method blank results (for the individual analyte) have numerical results above the existing MDL, then the existing MDL may optionally be left unchanged. Otherwise, adjust the MDL to the new verification MDL. (The range of 0.5 to 2.0

approximates the 95th percentile confidence interval for the initial MDL determination with six degrees of freedom.)

Addendum to Section II: Determination of the MDL for a Specific Matrix

The MDL may be determined in a specific sample matrix as well as in reagent water.

(1) Analyze the sample matrix to determine the native (background) concentration of the analyte(s) of interest.

(2) If the response for the native concentration is at a signal-to-noise ratio of approximately 5–20, determine the matrix-specific MDL according to Section 2 but without spiking additional analyte.

(3) Calculate MDL_b using the method blanks, not the sample matrix.

(4) If the signal-to-noise ratio is less than 5, then the analyte(s) should be spiked into the sample matrix to obtain a concentration that will give results with a signal-to-noise ratio of approximately 10–20.

(5) If the analytes(s) of interest have signal-to-noise ratio(s) greater than approximately 20, then the resulting MDL is likely to be biased high.

TABLE 1—SINGLE-TAILED 99th PERCENTILE t STATISTIC

Number of replicates	Degrees of freedom (n – 1)	t _(n – 1, 0.99)
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
32	31	2.453
48	47	2.408
50	49	2.405
61	60	2.390
64	63	2.387
80	79	2.374
96	95	2.366
100	99	2.365

III. Documentation

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. Data and calculations used to establish the MDL must

be able to be reconstructed upon request. The sample matrix used to determine the MDL must also be identified with MDL value. Document the mean spiked and recovered analyte levels with the MDL. The rationale for removal of outlier results, if any, must be

documented and maintained on file with the results of the MDL determination.

[FR Doc. 2017–17271 Filed 8–25–17; 8:45 am]

BILLING CODE 6560–50–P