ENVIRONMENTAL PROTECTION AGENCY

40 CFR Parts 136, 260, 423, 430, and 435

[EPA–HQ–OW–2010–0192; FRL–9664–6]

RIN 2040–AF09

Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures

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. EPA proposed these changes for public comment on September 23, 2010. The changes adopted in this final rule fall into the following categories: New and revised EPA methods and new and 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 process for EPA approval for use of alternate procedures for nationwide and Regional use; minimum quality control requirements to improve consistency across method versions; corrections to previously approved methods; and revisions to sample collection, preservation, and holding time requirements. Finally, EPA makes changes to three effluent guideline regulations.

DATES: This regulation is effective on June 18, 2012. The incorporation by reference of these methods is approved by the Director of the Federal Register on June 18, 2012. For judicial review purposes, this final rule is promulgated as of 1:00 p.m. (Eastern time) on June 1, 2012 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–2010–0192. All documents in the docket are listed on the *http://www.regulations.gov* Web site. Although listed in the index, some information is not publically available, *e.g.,* 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 *http://www.regulations.gov* or in hard copy at the HQ Water Docket Center, EPA/DC, EPA West, 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 is 202–566–2426 for the HQ Water Docket.

FOR FURTHER INFORMATION CONTACT: For information regarding the changes to inorganic chemical methods, contact Lemuel Walker, Engineering and Analysis Division (4303T), USEPA Office of Science and Technology, 1200 Pennsylvania Ave. NW., Washington, DC 20460, 202–566–1077 (email: *walker.lemuel@epa.gov*). For information regarding the changes to organic chemical methods, contact Maria Gomez-Taylor, Engineering and Analysis Division (4303T), USEPA Office of Science and Technology, 1200 Pennsylvania Ave. NW., Washington, DC 20460, 202–566–1005 (email: *gomez-taylor.maria@epa.gov*). For information regarding the changes to microbiological and whole effluent toxicity methods, contact Robin Oshiro, Engineering and Analysis Division (4303T), USEPA Office of Science and Technology, 1200 Pennsylvania Ave. NW., Washington, DC 20460, 202–566–1075 (email: *oshiro.robin@epa.gov*).

SUPPLEMENTARY INFORMATION:

A. General Information

1. Does this action apply to me?

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. Categories and entities that may potentially be affected by the requirements of today's rule include:

Category	Examples of potentially affected entities
State, Territorial, and Indian Tribal Governments.	States, Territories, and Tribes authorized to administer the NPDES permitting program; States, Territories, and Tribes providing certification under Clean Water Act section 401; State, Territorial, and Indian Tribal owned facilities that must conduct monitoring to comply with NPDES permits.
Industry	Facilities that must conduct monitoring to comply with NPDES permits.
Municipalities	POTWs or other municipality owned facilities that must conduct monitoring to comply with NPDES permits.

This table is not intended to be 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 today's 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 June 1, 2012 as provided at 40 CFR 23.2. The requirements of this regulation may also not be challenged later in civil or criminal proceedings brought by EPA.

C. Abbreviations and Acronyms Used in the Preamble and Final Rule

AOAC: AOAC International
ASTM: ASTM International
ATP: Alternate Test Procedure
CFR: Code of Federal Regulations
CWA: Clean Water Act
EPA: Environmental Protection Agency
FLAA: Flame Atomic Absorption Spectroscopy
HRGC: High Resolution Gas Chromatography
HRMS: High Resolution Mass Spectrometry
ICP/AES: Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP/MS: Inductively Coupled Plasma-Mass Spectrometry
ISO: International Organization for Standardization
MS: Mass Spectrometry
NIST: National Institute of Standards and Technology
NPDES: National Pollutant Discharge Elimination System
QA: Quality Assurance
QC: Quality Control
SDWA: Safe Drinking Water Act
SM: Standard Methods
SRM: Standard Reference Material
STGFAA: Stabilized Temperature Graphite Furnace Atomic Absorption Spectroscopy
USGS: United States Geological Survey
VCSB: Voluntary Consensus Standards Body
WET: Whole Effluent Toxicity

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I. Statutory Authority

EPA is promulgating today's rule pursuant to the authority of sections 301(a), 304(h), and 501(a) of the Clean Water Act (''CWA'' or the ''Act''), 33 U.S.C. 1311(a), 1314(h), 1361(a). Section 301(a) of the Act prohibits the discharge of any pollutant into navigable waters unless the discharge complies with a National Pollutant Discharge Elimination System (NPDES) permit issued under section 402 of the Act. Section 304(h) of the Act 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 this Act] or permit application pursuant to [section 402 of this Act].'' Section 501(a) of the Act authorizes the Administrator to ''* * * prescribe such regulations as are necessary to carry out this function under [the Act].'' 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 today's final rule.

A. New EPA Methods and New Versions of Previously Approved EPA Methods

This rule approves new EPA methods and new versions of already approved EPA methods. The following discussion briefly describes the EPA methods added today to Part 136.

1. Oil and grease. Today's rule adds a new version of EPA Method 1664, 1664 Revision B: 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 for use in CWA programs. Today, EPA is also amending the RCRA regulations at 40 CFR 260.11, which currently specify the use of Method 1664 Rev. A, to provide additionally for use of the revised version, 1664 Rev. B. As stated in the preamble to the proposal (75 FR 58026, Sept. 23, 2010), EPA encourages that future delistings cite ''Method 1664 Rev. B'' while delistings already granted may continue to use Method 1664 Rev. A.

On December 14, 2011, EPA published a notice of data availability (NODA) on a new method for oil and grease for use in Clean Water Act programs (see 76 FR 77742). This method, ASTM D–7575–10, uses a different extractant (a membrane filter instead of n-hexane for the extraction of oil and grease material) and a different measurement technique (infrared absorption instead of gravimetry) from the extractant and measurement technique of currently approved methods for oil and grease. The new method was discussed in the September 23, 2010 notice but EPA did not propose it for use as an approved method to be codified at 40 CFR 136.3 because oil and grease is a method-defined parameter. By definition, the measurement results of method-defined parameters are specific to the described method and are not directly comparable to results obtained by another method. However, since publication of the Methods Update Rule proposal, the Agency received additional data and information about this method and is re-considering whether it should add this method to the list of approved methods for oil and grease at 40 CFR 136.3. In the NODA, EPA proposed to include ASTM D–7575 for the measurement of oil and grease based on comments received in response to its September 23, 2010 proposal and the additional data. EPA will make a decision on the inclusion of the new method once it reviews the public comments received in response to the NODA and will then publish that decision in a separate **Federal Register** notice.

2. Metals. Today's rule adds EPA Method 200.5 (Revision 4.2): ''Determination of Trace Elements in Drinking Water by Axially Viewed Inductively Coupled Plasma—Atomic Emission Spectrometry'' to Table IB. The rule also clarifies that the axial orientation of the torch is allowed for use with EPA Method 200.7. Thus, EPA will allow the use of axial instruments or radial instruments to measure metals in water samples.

3. Pesticides. Today's rule adds EPA Method 525.2 to Table IG (Test Methods for Pesticide Active Ingredients) as an additional approved method for all parameters for which EPA has previously approved EPA Method 525.1, and also adds Methods 525.1 and 525.2 to Table ID for the same parameters for which EPA had previously approved Method 525.1 in Table IG. The rule also adds some of the methods for Pesticide Active Ingredients (Table IG) to applicable parameters listed in Table ID for general use. These methods are:

a. EPA Method 608.1, ''The Determination of Organochlorine Pesticides in Municipal and Industrial Wastewater.'' This method measures chlorobenzilate, chloroneb, chloropropylate, dibromochloropropane, etridiazole, PCNB, and propachlor.

b. EPA Method 608.2, ''The Determination of Certain Organochlorine Pesticides in Municipal and Industrial Wastewater.'' This method measures chlorothalonil, DCPA, dichloran, methoxychlor, and permethrin.

c. EPA Method 614, ''The Determination of Organophosphorus Pesticides in Municipal and Industrial Wastewater.'' This method measures azinphos methyl, demeton, diazinon, disulfoton, ethion, malathion, parathion methyl, and parathion ethyl.

d. EPA Method 614.1, ''The Determination of Organophosphorus Pesticides in Municipal and Industrial Wastewater.'' This method measures dioxathion, EPN, ethion, and terbufos.

e. EPA Method 615, ''The Determination of Chlorinated Herbicides in Municipal and Industrial Wastewater.'' This method measures 2,4-D, dalapon, 2,4-DB, dicamba, dichlorprop, dinoseb, MCPA, MCPP, 2,4,5-T, and 2,4,5-TP.

f. EPA Method 617, ''The Determination of Organohalide Pesticides and PCBs in Municipal and Industrial Wastewater.'' This method measures aldrin, α-BHC, β-BHC, γ-BHC (lindane), captan, carbophenothion, chlordane, 4,4′-DDD, 4,4′-DDE, 4,4′-DDT, dichloran, dicofol, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, isodrin, methoxychlor, mirex, PCNB, perthane, strobane, toxaphene, trifluralin, PCB-1016, PCB-1221, PCB-1232, PCB-1242, PCB-1248, PCB-1254, and PCB-1260.

g. EPA Method 619, ''The Determination of Triazine Pesticides in Municipal and Industrial Wastewater.'' This method measures ametryn, atraton, atrazine, prometon, prometryn, propazine, sec-bumeton, simetryn, simazine, terbuthylazine, and terbutryn.

h. EPA Method 622, ''The Determination of Organophosphorus Pesticides in Municipal and Industrial Wastewater.'' This method measures azinphos methyl, bolstar, chlorpyrifos, chlorpyrifos methyl, coumaphos, demeton, diazinon, dichlorvos, disulfoton, ethoprop, fensulfothion, fenthion, merphos, mevinphos, naled, parathion methyl, phorate, ronnel, stirofos, tokuthion, and trichloronate.

i. EPA Method 622.1, ''The Determination of Thiophosphate Pesticides in Municipal and Industrial Wastewater.'' This method measures aspon, dichlofenthion, famphur, fenitrothion, fonophos, phosmet, and thionazin.

j. EPA Method 632, ''The Determination of Carbamate and Urea Pesticides in Municipal and Industrial Wastewater.'' This method measures aminocarb, barban, carbaryl, carbofuran, chlorpropham, diuron, fenuron, fenuron-TCA, fluometuron, linuron, methiocarb, methomyl, mexacarbate, monuron, monuron-TCA, neburon, oxamyl, propham, propoxur, siduron, and swep.

4. Microbiologicals. Today's rule approves the 2005 versions of EPA Method 1622, ''Cryptosporidium in Water by Filtration/IMS/FA'' and EPA Method 1623, ''Cryptosporidium and Giardia in Water by Filtration/IMS/FA'' in Table IH for ambient water.

The rule approves revised versions of EPA Methods 1103.1, 1106.1, 1600, 1603, and 1680 in Table IH. The rule also approves the revised version of EPA Methods 1600, 1603 and 1680 in Table IA. We corrected technical errors in these revisions.

5. Non-Conventionals. Today's rule adds EPA Method 1627, ''Kinetic Test Method for the Prediction of Mine Drainage Quality'' to Table IB as a new parameter termed ''Acid Mine Drainage.''

6. Organics. Today's rule approves EPA Method 624, ''Purgeables,'' for the determination of acrolein and acrylonitrile in wastewater and revises footnote 4 to Table IC to specify that the laboratory must provide documentation about its ability to measure these analytes at the levels necessary to comply with associated regulations.

B. New Standard Methods and New Versions of Approved Standard Methods

This rule approves the following Standard Methods (SM) for certain pollutants currently listed in Table IB at Part 136. Laboratories performing measurements using any of the approved Standard Methods must follow the quality control (QC) procedures specified in the 20th or 21st edition of Standard Methods. Below is a list of the Standard Methods added to Table IB in Part 136:

1. SM 5520 B–2001 and SM 5520 F–2001, Oil and Grease, gravimetric
2. SM 4500–NH_3 G–1997, Ammonia (as N) and TKN, automated phenate method
3. SM 4500–B B–2000, Boron, curcumin method
4. SM 4140 B–1997, Inorganic Ions (Bromide, Chloride, Fluoride, Orthophosphate, and Sulfate), capillary ion electrophoresis with indirect UV detection
5. SM 3114 B–2009, Arsenic and Selenium, AA gaseous hydride
6. SM 3114 C–2009, Arsenic and Selenium, AA gaseous hydride
7. SM 3111 E–1999, Aluminum and Beryllium, direct aspiration atomic absorption spectrometry
8. SM 5220 B–1997, Chemical Oxygen Demand (COD), titrimetric
9. SM 3500–Cr B–2009, Chromium, colorimetric method
10. SM 4500–N_{org} D–1997, Kjeldahl Nitrogen, semi-automated block digestor colorimetric
11. SM 3112 B–2009, Mercury, cold vapor, manual
12. SM 4500–P G–1999 and SM 4500–P H–1999, Phosphorus, Total, automated ascorbic acid reduction
13. SM 4500–P E–1999 and SM 4500–P F–1999, Phosphorus, Total, manual, and automated ascorbic acid reduction
14. SM 4500–O B, D, E and F–2001, Oxygen, Dissolved, Winkler
15. SM 4500–O D–2001, Oxygen, Dissolved, Winkler

16. SM 4500–O E–2001, Oxygen, Dissolved, alum flocculation modification
17. SM 5530 B–2005, Phenols, manual distillation
18. SM 5530 D–2005, Phenols, colorimetric
19. SM 3500–K C–1997, Potassium, Total, selective electrode method
20. SM 2540 E–1997, Residues—Volatile, gravimetric
21. SM 4500–SiO_2 E–1997 and SM 4500–SiO_2 F–1997, Silica, Dissolved, automated molybdosilicate
22. SM 4500–SO_4^{2-} C–1997, D–1997, E–1997, F–1997 and G–1997, Sulfate, gravimetric, and automated colorimetric
23. SM 4500–S^{2-} B–2000 and C–2000, Sulfide, sample pretreatment

C. New ASTM Methods and New Versions of Previously Approved ASTM Methods

The rule approves the following ASTM methods for existing pollutants and ASTM methods for new pollutants to 40 CFR part 136, Table IB for inorganic compounds, and Table IC for organic compounds.

1. ASTM D2036–09 (B), Cyanide—Total, Cyanide amenable to cholorination
2. ASTM D6888–09, Cyanide—Available, flow injection and ligand exchange
3. ASTM D7284–08, Cyanide—Total, flow injection
4. ASTM D7511–09, Cyanide—Total, segmented flow injection
5. Free cyanide is added as a new parameter (24A in Table IB); two ASTM methods (D4282–02 and D7237–10) are approved, in addition to a new version of OIA 1677(2009) for this parameter. D4282–02 is a Standard Test Method for Determination of Free Cyanide in Water and Wastewater by Microdiffusion, and Method D7237–10 is a Standard Test Method for Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection.
6. ASTM D888–09 (A), Oxygen Dissolved, Winkler
7. ASTM D7573–09, Organic Carbon—Total, combustion
8. ASTM D7065–06, Five new chemicals in water: Nonylphenol (NP), Bisphenol A (BPA), p-tert-Octylphenol (OP), Nonylphenol Monoethoxylate (NP1EO), and Nonylphenol Diethoxylate (NP2EO), Gas Chromatography/Mass Spectrometry

D. New Alternate Test Procedures at 40 CFR 136.3

The rule approves eight 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 eight methods approved are added to Table IB:

1. Hach Company's Method 10360 Luminescence Measurement of Dissolved Oxygen in Water and Wastewater and for Use in the Determination of BOD_5 and $cBOD_5$, Revision 1.2 dated October 2011
2. In-Situ Incorporated's Method 1002–8–2009 Dissolved Oxygen Measurement by Optical Probe
3. In-Situ Incorporated's Method 1003–8–2009 Biochemical Demand (BOD) Measurement by Optical Probe
4. In-Situ Incorporated's Method 1004–8–2009 Carbonaceous Biochemical Oxygen Demand (CBOD) Measurement by Optical Probe
5. Mitchell Method M5271 dated July 31, 2008 for turbidity
6. Mitchell Method M5331 dated July 31, 2008 for turbidity
7. Thermo Scientific's Orion Method AQ4500 dated March 12, 2009 for turbidity
8. Easy (1–Reagent) Nitrate Method dated November 12, 2011 for nitrate, nitrite and combined nitrate/nitrite

E. Clarifications and Corrections to Previously Approved Methods in 40 CFR 136.3

The rule also clarifies the procedures for measuring orthophosphate and corrects typographical or other citation errors in Part 136. Specifically, the rule clarifies the purpose of the immediate filtration requirement in orthophosphate measurements (Table IB, parameter 44), which is to assess the dissolved or bio-available form of orthophosphorus (*i.e.,* that portion 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). EPA has added a footnote (24) to Table II providing this clarification. The rule also corrects missing citations to the table of microbiological methods for ambient water monitoring which are specified in Table IH at 40 CFR 136.3. When EPA approved the use of certain microbiological methods on March 26, 2007 (72 FR 14220), EPA inadvertently omitted fecal coliform, total coliform, and fecal streptococcus methods from the table. This omission is corrected in today's rule.

F. Revisions in Table II at 40 CFR 136.3(e) to Required Containers, Preservation Techniques, and Holding Times

The rule revises some of the current requirements in Table II at 136.3(e).

1. The rule revises footnote 4 of Table II to clarify the sample holding time for the Whole Effluent Toxicity (WET) samples for the three toxicity methods by adding the following sentence: ''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.'' In addition, EPA will post on the WET Web site corrections to errata in the ''Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms'' manual (EPA 2010e).

2. The rule revises the cyanide sample handling instructions in Footnote 5 of Table II to recommend the treatment options for samples containing oxidants described in ASTM's sample handling practice for cyanide samples, D7365–09a.

3. The rule revises the cyanide sample handling instructions in Footnote 6 of Table II to describe options available when the interference mitigation instructions in D7365–09a are not effective, and to allow the use of any technique for removal or suppression of interference, provided the laboratory demonstrates and documents that the alternate technique more accurately measures cyanide through quality control measures described in the analytical test method.

4. The rule revises footnote 16 of Table II instructions for handling Whole Effluent Toxicity (WET) samples by adding two sentences: ''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.''

5. The rule revises footnote 22 to Table II to read ''Sample analysis should begin as soon as possible after receipt; sample incubation must be started no later than 8 hours from time of collection.''

6. The rule adds three entries at the end of Table II with the containers, preservation, and holding times for the alkylated phenols, adsorbable organic halides, and chlorinated phenolics. When EPA proposed ASTM D7065–06 for the alkylated phenols, commenters noted that EPA did not include preservation and holding time information in Table II. When EPA moved EPA Methods 1650 and 1653

from 40 CFR part 430 to Table IC, EPA inadvertently omitted the associated parameters to Table II, and is correcting this omission in today's rule. The Table II information for containers, preservation, and holding times for these three new entries are taken from the approved methods.

G. Revisions to 40 CFR 136.4 and 136.5

This rule changes §§ 136.4 and 136.5 to clarify the procedures for obtaining review and approval for the use of alternate test procedures (alternate methods or ATPs) for those methods for which EPA has published an ATP protocol (there are published protocols for chemistry, radiochemical, and microbiological culture methods). In particular, it establishes separate sections outlining the procedures for obtaining EPA review and approval for nationwide use of an ATP (§§ 136.4), and the procedures for obtaining approval for limited use of an ATP (§§ 136.5).

In addition, this rule adds language to Part 136.5 to clarify the purpose and intent of limited use applications. This provision only allows use of an alternate method for a specific application at a facility or type of discharge. The Regional Alternate Test Procedure (ATP) Coordinator or the permitting authority, at his/her discretion, may grant approval to all discharges or facilities specified in the approval letter. However, the appropriate permitting authority within a state may request supporting test data from each discharger or facility prior to allowing any such approvals.

Today's rule further clarifies that the limited use provision cannot be used to gain nationwide approval and is not a way to avoid the full examination of comparability that is required for alternate test procedures when EPA considers a method for nationwide use with the ultimate goal of listing it as an approved CWA method at 40 CFR part 136. As further clarification, in the event that EPA decides not to approve a method proposed for nationwide use, the Regional ATP Coordinator or the permitting authority may choose to reconsider any previous limited use approvals of the alternate method. Based on this reconsideration, the Regional ATP Coordinator or the permitting authority will notify the user(s) if the limited use approval is withdrawn. Otherwise, the limited use approvals remain in effect.

H. Revisions to Method Modification Provisions at 40 CFR 136.6

This section allows users to make certain modifications to an approved method to address matrix interferences without the extensive review and approval process specified for an alternate test procedure at 136.4 and 136.5. Today's rule revises 136.6 to provide more examples of allowed and prohibited method modifications. The intent of today's revisions is to clarify those situations in which an ATP is required and those where it is not. Analysts may use the examples to help assess the need for a formal ATP, and in the event an ATP is not needed to document that their modification is acceptable and does not depart substantially from the chemical principles in the method being modified.

In response to comments, EPA has included additional examples of allowed and prohibited method modifications and has made some revisions to the text language as discussed in Section III below.

I. New Quality Assurance and Quality Control Language at 40 CFR 136.7

EPA is specifying ''essential'' quality control elements at § 136.7 for use in conducting an analysis for CWA compliance monitoring. This new language is added because auditors, co-regulators, laboratory personnel, and the regulated community have noted the variations in quality assurance (QA) and quality control (QC) procedures practiced by laboratories that use 40 CFR part 136 methods for compliance monitoring. Some of these methods are published by voluntary consensus standards bodies, such as the Standard Methods Committee, and ASTM International. Standard Methods and ASTM are available in printed or electronic compendia, or as individual online files. As mentioned in the proposal, each organization has a unique compendium structure. QA and QC method guidance or requirements may be listed directly in the approved consensus method, or, as is more often the case, these requirements are listed in other parts of the compendium.

Regardless of the publisher, edition, or source of an analytical method approved for CWA compliance monitoring, analysts must use suitable QA/QC procedures whether EPA or other method publishers have specified these procedures in a particular Part 136 method, or referenced these procedures by other means. These records must be kept in-house as part of the method testing documentation. Consequently, today's rule clarifies that an analyst using these consensus standard body methods for reporting under the CWA must also comply with the quality assurance and quality control requirements listed in the appropriate sections in that consensus standard body compendium. EPA's approval of use of these voluntary consensus standard body methods contemplated that any analysis using such methods would also meet the quality assurance and quality control requirements prescribed for the particular method. Thus, not following the applicable and appropriate quality assurance and quality control requirements of the respective method means that the analysis does not comply with the requirements in EPA's NPDES regulations to monitor in accordance with the procedures of 40 CFR part 136 for analysis of pollutants.

For methods that lack QA/QC requirements (as specified in this new section at 40 CFR 136.7), whether developed by EPA, a vendor, or a consensus standard body, analysts can refer to and follow the QA/QC published in several public sources. Examples of these sources include the relevant QA/QC sections of an equivalent approved EPA method, or voluntary consensus standards published as Part 136 approved methods (*e.g.,* Standard Methods, ASTM International, and AOAC). In addition to and regardless of the source of the laboratory's or method's QA and QC instructions, for methods that lack QA/QC requirements, EPA is adding requirements at 136.7 to specify twelve essential quality control elements that must be in the laboratory's documented quality system unless a written rationale is provided to explain why these quality control elements are inappropriate for a specific analytical method or application. These twelve essential quality control checks must be clearly documented in the written SOP (or method) along with a performance specification or description for each of the twelve checks, as applicable to the specific method. EPA has clarified the language in this section in response to public comments. The revised language is discussed in section III below.

J. Revisions at 40 CFR Part 423 (Steam Electric Power Generating Point Source Category)

The rule revises the 40 CFR part 423 definitions for total residual chlorine and free available chlorine at §§ 423.11(a) and 423.11(l) to allow the use of ''chlorine—total residual'' and ''chlorine—free available'' methods in § 136.3(a), Table IB, or other methods approved by the permitting authority.

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. EPA Is Not Adding EPA Method 1614A

The Agency proposed to add Method 1614A, ''Brominated Diphenyl Ethers in Water, Soil, Sediment, and Tissue by HRGC/HRMS.'' EPA developed this method to determine 49 polybrominated diphenyl ether (PBDE) congeners in aqueous, solid, tissue, and multi-phase matrices. This method uses isotope dilution and internal standard high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The commenters were divided on whether EPA should approve this method. Two commenters stated that Method 1614A would be a valuable addition to the list of approved methods, while two other commenters stated that the method has not been sufficiently validated for use in Clean Water Act programs. Upon further evaluation of the data supporting the use of this test procedure and the peer review comments, EPA agrees with those commenters who stated that additional validation data are needed to fully characterize the performance of this method for various matrices and has decided not to include Method 1614A in today's final rule.

B. Deferral of Action on EPA Method 1668C

The Agency proposed to add EPA Method 1668C, ''Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS.'' This method measures individual chlorinated biphenyl congeners in environmental samples by isotope dilution and internal standard high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). As discussed in the proposal, Part 136 methods for chlorinated biphenyls (PCBs) only measure a mixture of congeners in seven Aroclors—PCB–1016, PCB–1221, PCB–1232, PCB–1242, PCB–1248, PCB–1254, and PCB–1260, while Method 1668C can measure the 209 PCB congeners in these mixtures.

EPA began development of this method in 1995, initially covering 13 congeners labeled ''toxic'' by the World Health Organization. In 1999, EPA expanded the scope of the method to include all 209 PCB congeners. The method has been used to support several studies, including the 2001 National Sewage Sludge Survey and the National Lake Fish Tissue Survey. Since 1999, EPA has revised the method to incorporate additional information and data collected such as the results of an inter-laboratory validation study, peer reviews of the method and the validation study data, additional QC performance criteria and MDL data, and user experiences. In the development and subsequent multi-laboratory validation of this method, EPA evaluated method performance characteristics, such as selectivity, calibration, bias, precision, quantitation and detection limits. The Agency is aware that this method is being used in some states in their regulatory programs and by other groups for some projects with good success. For example, in a study of data comparability between two laboratories on samples collected from the Passaic River in New Jersey, in which 151 PCB congeners were identified and measured, accuracy, as measured by analysis of an NIST SRM, was 15% or better. Recoveries of the PCB congeners ranged from 90% to 124% and averaged 105%; precision ranged from 4.2 to 23% (Passaic River 2010). This type of data shows that recoveries and precision for this method are within the performance achievable with other approved methods.

EPA received comments from thirty-five individuals or organizations on this method. Of these commenters, five (three states, one laboratory, and one laboratory organization) supported the approval of this method. Some states indicated that they are already requiring this method for use in permits and for other purposes. On the other hand, industry and industry groups/associations were critical of the method for various reasons. Commenters opposing the method provided a detailed critique of the method, the inter-laboratory study, the peer reviews and the other supporting documentation. Among the criticisms of the inter-laboratory study, commenters argued that: (1) EPA did not produce documentation supporting changes to the method approved by EPA for the interlaboratory study, (2) the raw data for wastewater and biosolids was poor and is not fit for use in a comprehensive interlaboratory study, (3) EPA cited certain guidelines such as ASTM but deviated from those guidelines (*e.g.,* used only one Youden pair per matrix), (4) the peer reviewers' qualifications were questioned, (5) the addendum and the pooled MDLs/MLs were not subjected to peer review, (6) MDL/ML are flawed, the process to calculate MDLs/MLs for congeners that co-elute was flawed, the MDL/ML ignored the ubiquitous problem of background contamination, and (7) the validation study did not include all matrices in the method (soil and sediment excluded). In addition, some commenters also suggested that EPA should first promulgate new detection and quantitation procedures. Further, commenters raised questions about possible adverse effects of this new method on compliance monitoring as well as concerns about data reporting and costs.

EPA is still evaluating the large number of public comments and intends to make a determination on the approval of this method at a later date. In the meantime, the Agency has decided to go forward with the promulgation of the other proposed analytical methods to expedite their implementation by the regulated community and laboratories. This decision does not negate the merits of this method for the determination of PCB congeners in regulatory programs or for other purposes when analyses are performed by an experienced laboratory.

C. EPA Is Not Adding ASTM Methods D7574–09 and D7485–09

In today's rule, EPA is not adding two proposed ASTM methods, ASTM D7574–09 ''Standard Test Method for Determination of Bisphenol A (BPA),'' and ASTM D7485–09 ''Standard Test Method for Determination of NP, OP, NP1EO, and NP2EO.'' These two methods involve liquid chromatography and tandem mass spectrometry (LC/MS/MS). The methods have been tested by a single laboratory in several environmental waters, and may be useful for many applications. However, EPA has decided to postpone approval of these two methods for general use until completion of a full inter-laboratory validation study designed to fully characterize the performance of these methods across multiple laboratories and matrices.

D. Revisions and Clarifications to EPA Method 200.7

EPA Method 200.5 ''Determination of Trace Elements in Drinking Water by Axially Viewed Inductively Coupled Plasma—Atomic Emission Spectrometry'' employs a plasma torch viewed in the axial orientation to measure chemical elements (metals). As stated earlier in today's rule, EPA is adding Method 200.5 for some metals in Table IB. Both Methods 200.5 and 200.7 are acceptable methods under Part 136 and both methods employ ICP/AES technology. However, Method 200.5 includes performance data for the axial configuration that is not in Method 200.7 because the axial technology torch results were not available when Method 200.7 was developed. For some parameters listed in Table IB, the axial orientation using ICP/AES technology results in greater sensitivity and lower detection limits than the radial orientation. Thus, today's approval of Method 200.5 and the additional flexibility to modify Method 200.7 to use the axial orientation discussed in the proposal will allow laboratories to use either axial instruments or radial instruments to measure metals in water samples with Method 200.7. In response to EPA's proposal to allow the use of the axial orientation of the torch with EPA Method 200.7, commenters expressed support for this added flexibility. Thus, today's rule clarifies that the use of the axial orientation of the torch to measure metals is an acceptable modification to Method 200.7. EPA has added new text at Part 136.6(b)(5) to allow the use of the axial orientation of the torch for Method 200.7 as an acceptable method modification that does not require an ATP application.

EPA further notes that there was a typographical error in Section II.J of the proposed rule which stated that the version of EPA Method 200.7 (which the Agency proposed to remove; with Appendix C, see section IIIM below) has been superseded by Revision 5.4 of Method 200.7. Today's final rule reflects that the correct reference is Revision 4.4 of EPA Method 200.7. In today's rule, EPA has added Method 200.7 Revision 4.4 as an additional approved method for the measurement of titanium. As some commenters pointed out, EPA Method 200.7 covers this parameter and exclusion of this method for the measurement of titanium in Table IB was an oversight.

In addition, EPA has removed EPA Method 200.7 from Table IB for the measurement of mercury. The addition of EPA Method 200.7 to the list of approved methods for mercury in Table IB was an error. Although this pollutant is on the list of analytes in EPA Method 200.7, mercury may be lost to the atmosphere through the use of the approved total recoverable metals digestion procedures (*e.g.,* EPA Method 200.2, or the digestion procedures listed in EPA Method 200.7) that must be applied to the wastewater samples of interest under the Clean Water Act program. Such losses can lead to poor recovery in the samples compared to the sample preparation procedures included in other mercury methods approved at 40 CFR part 136. Therefore, EPA Method 200.7 has not been included in Table IB for mercury.

E. Revisions and Corrections to Certain Citations in Tables IA, IB, IC, ID, and IG

EPA proposed some additions to Table IB which include some new Standard Methods or new versions of approved Standard Methods. Today's rule revises the applicability of some methods and makes some corrections to the method citations. Specifically, EPA removed SM 3120 and SM 3125 for the measurement of mercury because mercury is not on the list of analytes for these methods. In addition, EPA corrected the citation of SM 3113 to SM 3113B–2004 in the final rule and has added SM 3113B–2004 for the measurement of cadmium, chromium, iron, lead, and silver, because these analytes are covered by the method and they exhibit acceptable analytical performance. These omissions were an oversight.

EPA also deleted from Table ID an EPA GC/MS method, Method 525.1, for the measurement of ametryn, diazinon, disulfoton, prometon, and trifluoralin. These analytes are not listed within the scope of this method and their inclusion in the proposal was an error.

EPA has corrected a number of typographical errors in the tables and footnotes, correcting spelling and method availability information, method title names, and document identification numbers. A complete list of these changes has been included in a memo to the docket.

F. Continued Approval of Method 1664 Rev. A

EPA proposed to replace Method 1664 Rev. A for the measurement of oil and grease with a revised version (Method 1664 Rev. B). This new version of the method describes modifications that are allowed and modifications that are not allowed when using this method for compliance with Clean Water Act regulations. Comments were generally supportive of the revised method but some commenters recommended that Method 1664 Rev. A not be withdrawn immediately because many permits currently specify the use of this method. In response to these comments, EPA will continue to allow the use of Method 1664 Rev. A for current permits because this method is not significantly different from the revised version of the method. However, EPA strongly encourages the use of the revised method (Method 1664 Rev. B) in the future. EPA may revisit this decision in a future rulemaking.

G. Revision to Footnote 63 of Table IB at 40 CFR 136.3

EPA received comments that the Hach Method 10360, described in footnote 63 of Table IB, is a dissolved oxygen procedure, and as such, should only be listed as a procedure for dissolved oxygen, and not for BOD and CBOD. EPA disagrees with these commenters because the method on its face is clearly applicable to dissolved oxygen measurements in conjunction with BOD and CBOD analyses, as described in the method. As a result, in today's final rule, EPA added language to the end of this footnote to clarify that Part 136 allows the use of Hach Method 10360 for measurement of dissolved oxygen in conjunction with the methods approved for measurement of biochemical demand (BOD) and carbonaceous biochemical oxygen demand (CBOD).

H. Revision to Footnote 4 of Table IC at 40 CFR 136.3

EPA received comments on the proposed approval of Method 624 for the definitive determination of acrolein and acrylonitrile. Commenters agreed with the addition of these two analytes, but one of these commenters expressed concern about a blanket approval without requiring a demonstration of adequate performance and appropriate sample introduction techniques. This commenter recommended that performance criteria and information about appropriate sample introduction techniques be added to footnote 4 of Table IC. EPA agrees with this commenter's suggestions because this requirement would ensure that the laboratory has the ability to measure these analytes at the levels necessary to comply with any associated regulations. In response to these concerns, in today's rule, the Agency revised the footnote to add a statement requiring documentation of the ability to quantitatively measure these analytes and advising analysts that other sample introduction techniques may be required to achieve adequate performance.

I. Revisions to Table II Language

EPA proposed to revise the text at 136.3(e) to allow any party to modify sample preservation and holding times after submitting documentation to its permitting or other authority that supports use of an alternative approach. Commenters expressed concern that this change would present a burden both to permitting authorities to review and approve changes, and for laboratories that work in different states because each state could have different requirements. In response to public comments, EPA has removed the proposed language at 136.3(e) that would have allowed such modifications based on documentation and procedures determined by individual permitting authorities. Instead, such modifications must continue to be requested via a limited use ATP application to the Regional Alternate Test Procedure Coordinator or permitting authority, as appropriate. Thus, approval of any changes in sample preservation procedures, container materials, and maximum allowable holding time will remain unchanged and continue to be the responsibility of EPA through its Alternate Test Procedure program. EPA clarified language regarding the limited use application process procedure. Additionally, in today's rule, EPA added a clarifying sentence at the end of the current language to emphasize that an analyst cannot modify any sample preservation or holding time requirements in an approved method unless the requirements in Section 136.3(e) are met.

EPA also revised footnote 4 to Table II to delete the parenthetical statement specifying that samples analyzed for fecal coliforms may be held up to six hours prior to commencing analysis. That statement in footnote 4 is inconsistent with the requirement for an eight-hour holding time, as pointed out by a commenter.

In response to comments, EPA included a new entry in Table II for the alkylated phenols (parameters 114 to 118 in Table IC) that was inadvertently omitted from the proposal. Similarly, when EPA moved EPA Methods 1650 and 1653 to Table IC, EPA inadvertently omitted to add the parameters adsorbable organic halides (AOX) and chlorinated phenolics to Table II. The Table II information for containers, preservation, and holding times for these three new entries are taken from the approved methods.

J. Approval of Alternate Test Procedures for Limited Use at 40 CFR 136.5

EPA proposed changes to 40 CFR 136.4 and 136.5 that establish the procedures for obtaining approval for use of a nationwide or limited use ATP. The proposed revisions established separate sections outlining the procedures for obtaining EPA review and approval for nationwide use of an ATP (§§ 136.4), and the procedures for obtaining approval for limited use of an ATP (§§ 136.5). The proposal also included language to clarify that limited use approvals do not require the same level of supporting data that would be required for nationwide approvals and that limited use approvals are not intended to be used as a means to avoid the full examination of comparability that is required for an application for approval of an alternative test procedure for nationwide use.

Today's rule finalizes these sections as proposed with one exception. EPA received comments that the proposed language under § 136.5 does not require that comparability data be submitted when seeking a Regional limited use ATP approval. EPA agrees that comparability data is an essential component of the ATP approval process and had inadvertently omitted this language. As a result, the Agency added language in today's final rule that requires an applicant to provide comparability data specific to the limited use for the performance of the proposed alternative test procedure relative to the performance of the reference method.

K. Revisions to Language at § 136.6

EPA proposed to revise the section on method modification provisions at 40 CFR 136.6 to provide more examples of allowed and prohibited method modifications. Acceptable reasons for an analyst to modify a method include analytical practices that lower detection limits, improve precision, reduce interferences, lower laboratory costs, and promote environmental stewardship by reducing generation of laboratory wastes. Acceptable modifications may use existing or emerging analytical technologies that achieve these ends provided that they do not depart substantially from the underlying chemical principles in methods currently approved in 40 CFR part 136. Analysts may use the examples in this section to help assess whether the modifications require an ATP and if not, to document that their modification is acceptable. The additional examples provide further guidance to laboratories and permittees on allowable method modifications that do not require an application through the ATP program. Proposal comments generally expressed support for allowing the flexibility to make certain changes to methods and for the specific examples of allowable changes included in the proposal. In addition, some commenters suggested revisions to clarify EPA's intent in Sections (b)(4) and (b)(5) of 40 CFR 136.6. EPA reviewed the suggestions and agrees with commenters that the revisions will provide additional clarity. In addition, as discussed in Section III.D of this preamble, EPA added the use of axially viewed torch as an allowable modification to Method 200.7. Today's rule includes the following revisions to the regulatory text:

(a) Adds language to Section (b)(3) to clarify that modifications to sample collection, preservation, and holding time do not fall within the scope of 136.6,

(b) Revises the language at (b)(4)(T) be more specific with respect to the use of gas diffusion across a hydrophobic semi-permeable membrane to separate the analyte of interest from the sample matrix in place of manual or automated distillation for the analysis of certain analytes,

(c) Revises the equation for Relative Standard Error (RSE) in (b)(4)(J) to make it consistent with the description in other EPA methods, and

(d) Adds the use of an axially viewed torch with Method 200.7 as an allowable modification.

L. Revisions to New Quality Assurance and Quality Control Language

For today's rule, EPA added some introductory language to this section to clarify the new requirements. EPA added this language to provide some additional clarity as to when the new requirements are applicable and, thus, must be incorporated into the laboratory's documented standard operating procedures. Additional discussion of the revisions is provided under section IV.C below.

M. Withdrawal of Appendices at 40 CFR Part 136

EPA proposed to incorporate by reference in Table IB all of the methods printed in 40 CFR part 136 Appendices A and C, and to remove most of the information in Appendix D. The methods in Appendix A are EPA Method Numbers 601 through 613, 624, 625, 1613B, 1624B, and 1625B. Appendix C contains EPA Method 200.7, ''Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma—Atomic Emission Spectrometry''. However, Federal regulations at 1 CFR part 51.7(c)(1) prohibit the incorporation by reference of material previously published in the **Federal Register**. Thus, EPA is not withdrawing Appendices A or C. Because EPA Method 200.7 has been revised, EPA is replacing the current version of this method in Appendix C with Rev. 4.4 of Method 200.7. All of these methods are readily accessible from a variety of sources, including EPA's CWA methods Web site *http://water.epa.gov/scitech/methods/cwa/index.cfm.*

The rule also removes most of the data from Appendix D for all EPA methods that are no longer approved, and retains only the Precision and Recovery Statements for EPA Method 279.2 for thallium and EPA Method 289.2 for zinc, and corrects typographical errors in the Appendix. The current version of Appendix D will be available online at the CWA methods Web site for historical purposes.

N. Revisions at 40 CFR Part 430 (Pulp, Paper, and Paperboard Point Source Category)

EPA also proposed to remove Appendix A at 40 CFR part 430 and to incorporate by reference the methods in this Appendix. Appendix A contains two methods, EPA Method 1650 for adsorbable organic halides or AOX, and EPA Method 1653 for chlorinated phenolics. As explained above, we cannot incorporate by reference this material, so Appendix A remains unchanged in the Code of Federal Regulations. These methods are also readily available from a variety of sources, including EPA's CWA methods Web site *http://water.epa.gov/scitech/methods/cwa/index.cfm*. EPA is also adding these two methods to Table IC for general use.

O. Revisions at 40 CFR Part 435 (Oil and Gas Extraction Point Source Category)

The rule makes several changes to Part 435, Oil and Gas Extraction Point Source Category. First, EPA is moving the methods and associated quality assurance requirements from 40 CFR part 435, Subpart A (Offshore Subcategory) to an EPA document (''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004), and incorporating by reference this document in the revised regulation at 40 CFR part 435. This approach organizes the analytical methods for the Offshore Subcategory into one document and allows for easier access to the methods for this category. The following table lists the methods EPA moved from part 435 to the cited document, EPA–821–R–11–004.

EPA METHOD NUMBERS FOR OIL AND GAS EXTRACTION POINT SOURCE CATEGORY ANALYTICAL METHODS AND PRIOR CFR REFERENCES

Analytical/Test method	EPA Method No.	Date first promulgated	Previous CFR references
Static Sheen Test	1617	1993	Subpart A, Appendix 1.
Drilling Fluids Toxicity Test	1619	1993	Subpart A, Appendix 2.
Procedure for Mixing Base Fluids With Sediments	1646	2001	Subpart A, Appendix 3.
Protocol for the Determination of Degradation of Non-Aqueous Base Fluids in a Marine Closed Bottle Biodegradation Test System: Modified ISO 11734:1995.	1647	2001	Subpart A, Appendix 4.
Determination of Crude Oil Contamination in Non-Aqueous Drilling Fluids by Gas Chromatography/Mass Spectrometry (GC/MS).	1655	2001	Subpart A, Appendix 5.
Reverse Phase Extraction (RPE) Method for Detection of Oil Contamination in Non-Aqueous Drilling Fluids (NAF).	1670	2001	Subpart A, Appendix 6.
Determination of the Amount of Non-Aqueous Drilling Fluid (NAF) Base Fluid from Drill Cuttings by a Retort Chamber (Derived from API Recommended Practice 13B–2).	1674	2001	Subpart A, Appendix 7.

As noticed in the proposed rule, EPA is also incorporating additional quality assurance procedures in the marine anaerobic biodegradation method (Appendix 4 of Subpart A of part 435) and is correcting some erroneous references and omissions in the method for identification of crude oil contamination (Appendix 5 of Subpart A of part 435) into the new document (EPA–821–R–11–004).

EPA promulgated the use of the marine anaerobic biodegradation method (closed bottle test, ISO 11734:1995 as clarified by Appendix 4 to Subpart A of part 435) as an Appendix to the rule in 2001 because it most closely modeled the ability of a drilling fluid to biodegrade anaerobically in marine environments (January 22, 2001; 66 FR 6864). Subsequent to this promulgation, EPA incorporated additional quality assurance procedures for the marine anaerobic biodegradation method in the NPDES permit for the Western Gulf of Mexico (''Final NPDES General Permit for New and Existing Sources and New Dischargers in the Offshore Subcategory of the Oil and Gas Extraction Category for the Western Portion of the Outer Continental Shelf of the Gulf of Mexico,'' GMG290000, Appendix B). The additional quality assurance instructions in the GMG290000 more clearly describe the sample preparation and compliance determination steps. Specifically, these additional quality assurance procedures clarify that users must only use headspace gas to determine compliance with the Part 435 effluent guidelines. EPA worked with the same industry consortium that assisted EPA in the development of the analytical methods used in the effluent guidelines for the Oil and Gas Extraction point source category (40 CFR part 435) to develop these additional quality assurance measures. Thus, the quality assurance procedures are generally applicable to this industry.

Additionally, as noticed in the proposed rule, EPA is correcting some erroneous references and omissions in the method for identification of crude oil contamination (Appendix 5 of Subpart A of Part 435), as follows:

a. Adding a schematic flow for qualitative identification of crude oil, which was erroneously omitted in Appendix 5 to Subpart A of part 435,

b. Correcting erroneous citations in sections 9.5, 9.6, 11.3, and 11.3.1 of Appendix 5, and

c. Adding a missing ''<'' (less than) sign for identification of crude oil contamination in the asphaltene crude discussion at Section 11.5.4.2. The asphaltene discussion now reads as follows: ''Asphaltene crude oils with API gravity < 20 may not produce chromatographic peaks strong enough to show contamination at levels of the calibration. Extracted ion peaks should be easier to see than increased intensities for the C8 to C13 peaks. If a sample of asphaltene crude from the formation is available, a calibration standard shall be prepared.''

EPA received three comments on the proposed changes. One commenter was concerned that the EPA document (EPA–821–R–11–004) would not have the same legal status as publishing the methods in the CFR. EPA disagrees with this comment. The incorporation by reference of this document has the same legal standing as publishing the text of the methods in the CFR. EPA has a long standing practice of publishing test methods using incorporation by reference and the cited test methods are as legally enforceable as those published in full in the CFR. EPA is consolidating these methods into one document to allow for easier access to these methods. The incorporation by reference of this document also allows for better formatting of the methods and eliminates the redundant publication of these methods each year in the Code of Federal Regulations. Two other commenters had some recommendations for additional revisions to the EPA document (EPA–821–R–09–013). EPA has not adopted these suggestions, given the absence of an opportunity for the public generally to comment on them. EPA will, however, consider these comments and may propose additional revisions in a future rulemaking. As noticed in the proposed rulemaking, the final rule consolidates the oil and gas test methods into a single document and references this document in the effluent guidelines (40 CFR part 435). Like any other changes to an EPA-approved method, any changes to the methods in the EPA document (EPA–821–R–11–004) will require a rulemaking.

IV. Summary of EPA's Response to Comments

The Agency received comments from 117 different individuals or organizations on the September 23, 2010 proposal (75 FR 58024). Commenters represented a variety of different interests, including analytical laboratories, water utilities, instrument manufacturers, State and local governments, trade associations, and industry. A summary of major public comments on the proposed rule and the Agency's responses is presented in this section. The public docket for this rule includes all of the comments received and the Agency's responses.

A. Approval of Standard Methods

EPA proposed to revise how to identify EPA-approved Part 136 methods that are published by the Standard Methods Committee (*i.e.,* Standard Methods). EPA proposed two changes. First, EPA proposed to change the way it identifies an EPA-approved version of a Standard Method in Part 136. Second, EPA proposed to identify only the most recently EPA-approved version of a Standard Method in Part 136. In the past, EPA listed multiple versions of these methods from the 18th, 19th, 20th editions of the printed compendiums, or from the on-line editions published by the Standard Methods Committee, in one or more columns in the Part 136.3 tables. In some cases, EPA approved more than one version of a Standard Method for a particular analyte in Part 136. Approval of several versions of the same Standard Method for an analyte has led to inconsistencies in how laboratories conduct these analyses, especially in quality assurance/quality control (QA/QC) practices. For this reason, EPA proposed to list only the most recently EPA-approved version of a Standard Method (regardless of the printed or on-line edition) in Part 136, with few exceptions, to identify the method with the year of Standard Methods approval or adoption designated by the last four digits in the method number (*e.g.,* Standard Method 3113B–2004). This approach clearly identifies the version of the standard method approved under Part 136 and no longer ties it to a particular compendium printing or edition of Standard Methods. For example, the exact method, Standard Method 3113B–2004 appears in the 18th, 19th, and 20th edition of Standard Methods. Because this method is the same in all of these editions, a laboratory may refer to any of these editions when using Standard Method 3113B–2004 to measure the analytes listed in Table IB that are approved for this method. Thus, EPA's proposed approach to identify Part 136 approved standard methods does not rely on the particular edition of a compendium but rather on the latest Standard Methods approved version (by indicating the year of approval).

EPA received numerous comments concerning the proposed changes to specify the method with the year of publication, rather than specifying the editions of Standard Methods in which the method is printed, and to list in Part 136 only the most recent EPA-approved version of a Standard Method if Standard Methods has multiple versions of a method for a pollutant. Some commenters expressed concern about other economic impacts related to laboratory start-up tests, and the need for training and revised standard operating procedures (SOPs) associated with the use of the most recently approved method. In response, EPA maintains that the economic impacts of start-up tests or the need for revised SOPs are part of the necessary expenses to maintain a laboratory producing data of known and acceptable quality and these costs are not unusual. Training new staff or training current staff on new procedures is also a cost that any laboratory must consider as part of doing business.

EPA is aware that Standard Methods and other voluntary consensus organizations such as ASTM and AOAC periodically revise existing methods and publish them on-line and/or as a compendium. In addition to EPA-developed methods, the Agency approves certain methods developed by these and other organizations as required under the National Technology Transfer and Advancement Act (NTTAA) and lists them in Part 136 periodically. Often, after EPA approves a Standard Method for use in Part 136, Standard Methods releases or adopts a revised version of that method. Generally, these revised Standard Methods involve the use of new technologies or improvements to previously approved methods. By referencing the year of adoption by Standard Methods, EPA's proposed change in its method citations was intended to clarify which version of a Standard Method is approved by EPA in Part 136. The on-line site for Standard Methods allows electronic release of new methods and revisions to existing methods prior to the publication of the compendium edition. Currently, Standard Methods is on a 5–7 year cycle for publication of the compendium and is set to release its 22nd edition soon. In some cases, an older version of a method approved by the Standard Methods Committee may appear on the on-line or compendium version of Standard Methods. The date of adoption is on the first page of the compendium or on-line method.

Commenters are correct in pointing out that, in the event that they elect to use an EPA-approved Standard Method for compliance purposes, they would be required to use the most recently EPA-approved version of a Standard Method. EPA is not requiring any EPA-approved Standard Method in today's rule. Dischargers may use any approved Part 136 method for compliance monitoring unless the method is specified in its discharge permit by the permitting authority, or the method is not sufficiently sensitive to comply with the permit limit. Also, if the discharger elects to use an EPA-approved Standard Method and does not have the most recent EPA-approved version, EPA finds the costs would not be significant. The discharger/laboratory would need to purchase the on-line version for the individual method and would not need to absorb the cost of a full subscription to the on-line service. On-line versions of a single method generally cost $69. Relative to the costs that laboratories charge to run such an analysis (generally many times over), this cost is negligible. Therefore, EPA does not agree with commenters that they will have to purchase an on-line subscription to Standard Methods nor does it conclude that this change will present a significant financial burden to laboratories.

Another concern raised was that any changes in Standard Methods in the future would be automatically approved without EPA review. This assertion is incorrect. Any new or revised Standard Methods would be proposed in the **Federal Register** for public comment before inclusion in Part 136 as required under the Clean Water Act.

Some commenters also expressed concern that this change may affect the approval status of existing alternate test procedures that were evaluated by EPA relative to older Standard Methods. With respect to this concern, the Agency is not withdrawing any approved ATPs. EPA's withdrawal of its earlier approved versions of Standard Methods is not intended to affect the acceptance of any vendor-developed methods based on older Standard Methods that EPA previously determined to be acceptable versions, because the changes in Standard Methods are mostly editorial (*e.g.,* clarifications, increased flexibility) and not procedural changes.

In making this change in today's rule, EPA also considered that beginning with the publication of the 20th edition of Standard Methods, the Standard Methods Committee included the quality control (QC) procedures which are similar to the QC procedures that have been included by EPA in methods published in Part 136 over the last two decades for use in compliance monitoring programs under the Clean Water Act and the Safe Drinking Water Act. These procedures are specified in Part 1000 of the Standard Methods compendium and include the ''essential'' quality control checks that EPA has added at 40 CFR 136.7 as part of this final rule.

B. Preservation and Holding Time Requirements for EPA Method 624

In response to the proposed use of EPA Method 624 as a definitive measurement method for acrolein and acrylonitrile, EPA received comments on the preservation and holding time requirements for these two pollutants. Commenters noted that the preservation and holding time requirements in Part 136 Table II for these two analytes currently differ from the requirements for other Method 624 analytes. Historically, these two analytes have had different preservation and requirements than the analytes currently listed in EPA Method 624. The current requirements in Table II date to 1984 and specify that samples for acrolein and acrylonitrile must be preserved at a pH in the range of 4 to 5. This pH range is based on concerns about degradation of these two analytes in strongly acidic samples (*e.g.,* pH < 2). Footnote 10 to Table II currently states that pH adjustment is not required if acrolein will not be measured, but that samples for acrolein receiving no pH adjustment at all must be analyzed within 3 days of sampling. In contrast, samples to be analyzed by EPA Method 624 for purgeable halocarbons are not preserved by adjusting the pH, and samples to be analyzed for the purgeable aromatic hydrocarbons (benzene, ethylbenzene and toluene) are preserved at a pH of 2. Thus, in the case where a permittee wants to use EPA Method 624 to measure acrolein or acrylonitrile in addition to other analytes included in Method 624, the sampler has to take an additional sample, preserve the sample for acrolein and acrylonitrile to pH 4 to 5, and then perform separate analyses. Commenters stated that EPA does not have a basis for requiring a different preservation and holding times for these two analytes and submitted data that support their assertion that sample preservation be allowed at either a pH of 7 or a pH of 2. EPA has reviewed the data, but the Agency has concluded that these data are not sufficient or compelling to change the current preservation and holding time requirements for these analytes because the data are anecdotal rather than the result of a well-planned and properly documented stability study. As a result, EPA's final rule retains the current sample preservation and holding time requirements for acrolein and acrylonitrile.

C. Quality Assurance and Quality Control Requirements

EPA proposed to specify minimal essential quality control requirements at Part 136.7 for use in conducting analyses to comply with CWA monitoring requirements. The purpose of this requirement is to ensure that laboratories conducting CWA compliance monitoring use suitable QA/QC procedures. These QA/QC procedures were included in a memorandum to EPA's Regional Quality Assurance Managers (May 7, 2009 memorandum from Richard Reding) and have been posted on EPA's Web page since 2009. These requirements do not apply in the case of the use of Part 136 approved methods that contain (or reference) their own QA/QC procedures, or to any non-compliance analyses. Most analytical methods currently listed in Part 136 contain QA/QC procedures, and permittees/laboratories using those methods are not affected by the new requirement. However, there are a few older methods approved for use in Part 136 from the 1970s that contain no QA/QC requirements. Examples of Part 136 methods that lack QA/QC are Method 283.2 for titanium and Method 289.2 for zinc, both furnace atomic absorption methods issued in 1978. As explained previously, an additional issue identified in the May 7, 2009 memorandum is that approved methods from consensus organizations such as Standard Methods contain the QA/QC requirements in a different section of their methods compendium (*e.g.,* Standard Methods consolidates general QA/QC requirements for all methods in Part 1000 of their methods compendium). Thus, EPA wants to clarify that it expects permittees/laboratories using Part 136 approved methods developed by consensus organizations for reporting compliance under the CWA to also comply with the QA/QC requirements listed in the appropriate sections in that consensus organization's compendium.

In addition to following QA/QC requirements from consensus organizations for Part 136 methods without QA/QC procedures, the analyst has the option to follow the QA/QC published in another EPA-approved method for that parameter that contains such QA/QC.

As discussed in Section II.I of this preamble, EPA is reiterating the requirement to include QA/QC in any chemical method used for CWA compliance purposes. For those few Part 136 methods that lack QA/QC requirements, EPA is adding quality control requirements at § 136.7. EPA received numerous comments on this aspect of the proposed rule. Although some commenters expressed support for EPA's intent to ensure the quality of data by adding the new QC language, many commenters noted problems with the specific language, including that many of the QC elements do not apply to common parameters (*e.g.,* MDLs cannot be calculated for pH or BOD, and surrogates and internal standards have no counterparts in microbiological methods). Other commenters expressed concern that the new language was either duplicative or contradicted language in existing EPA-approved methods, or presented conflicts with various state or national accreditation programs. Other commenters objected to the perceived costs associated with this new requirement and suggested that the QC checks simply will not occur, regardless of the new Part 136.7 requirement. A few commenters suggested improvements to the proposed language, should EPA decide to proceed with this new section. One commenter stated that the section was not needed, since EPA should not be approving methods at 40 CFR part 136 that do not already contain appropriate QA/QC. EPA addresses these issues below.

With respect to the issue of applicability of the QC elements, EPA agrees with commenters who stated that some QC elements listed in § 136.7 may not apply to common parameters (*e.g.,* matrix spike and matrix spike duplicates do not apply to pH measurements). For any of the Part 136 methods that include (or reference) appropriate QC elements for these parameters, these new QA/QC requirements are not applicable. As a result, in today's final rule, EPA has added introductory language in § 136.7 to clarify how laboratories should comply with this new requirement when one or more of the twelve essential quality control elements is not applicable to a method. This new introductory language states that in cases where one or more of the twelve QC elements do not apply to a given method, the laboratory may provide a written rationale for not including those elements in their standard operating procedures (SOP) for that analysis. This may be something as simple as stating that the given QC element does not apply to that analysis or is not possible to perform (as the example above for pH measurements). In addition, the final rule states that the twelve QC elements, as applicable, must be included in a laboratory's SOP for conducting an analysis with an approved method only when there are no QA/QC procedures in the Part 136 method. Again, as discussed above, this QA/QC requirement at Part 136 does not apply to approved methods containing (or referencing) QA/QC procedures.

In response to the comment that the language is either duplicative or contradicted in existing approved methods or accreditation programs, EPA has added this new section to the regulations at Part 136.7 to address concerns that certain approved methods do not contain QA/QC procedures. In those cases where an approved method incorporates these QC procedures (as applicable to that method), the laboratory can follow the method as written without creating any duplication or conflict. As mentioned in Section IV.A of this preamble, Standard Methods incorporated new QC requirements starting with the 20th edition of Standard Methods similar to the QC requirements included in EPA methods for the last two decades. Thus, most Standard Methods that are also approved methods in Part 136 already contain QA/QC requirements, as applicable. Similarly, EPA does not anticipate conflicts with laboratory accreditation programs because these programs generally follow the QC requirements in the method or as otherwise specified in regulatory programs. The purpose of this new section is to ensure that analyses conducted for compliance monitoring with CWA regulatory programs contain appropriate QA/QC and the Agency's view is that this is already occurring in most laboratories (with a few exceptions as discussed above). This new requirement is added to clarify that laboratories must implement proper QA/QC, as needed, for all CWA compliance related analyses to provide quality data that will withstand regulatory and legal challenges.

In response to the comment that this new requirement will be costly, proper QA/QC is essential for obtaining results of known and acceptable quality. In the long run, it could be much more costly to use data which lacks proper QC in demonstrating or enforcing discharge requirements. In the short run, laboratories would only incur costs associated with this new requirement when the method lacks QA/QC and when they have not included QA/QC as part of their SOPs. EPA estimates that this would not have a significant impact on laboratories because the vast majority of Part 136 methods already include or reference QA/QC requirements. Further, most laboratories already implement the QC checks prescribed by the newer methods and are already documenting these QC checks in the laboratory SOPs. Some of the QC checks are a one-time or infrequent expense (*e.g.,* demonstration of capability and determination of a method detection limit), while other checks are routine (*e.g.,* running a method blank). Typically, laboratories include QC as part of the overall analysis costs, and these costs generally add 10–20% to the analysis cost initially for an analyst demonstration of capability, and less (5–10%) after the initial cost for routine QC (*e.g.,* running a blank with every batch of samples). For a typical analysis of a metal using furnace atomic absorption, at a cost of $35–50 per sample, the QC costs would be typically 5–10% of the total costs, and are generally included in the laboratory pricing schedule. Thus, EPA expects that any costs associated with this aspect of today's rule will be minimal and limited to a few older methods that some laboratories may still elect to use rather than the many other methods that contain QA/QC requirements. EPA considers these QC checks to be an essential part of an overall approach to producing data of known quality and defensibility when a particular method is used to measure pollutants for compliance monitoring purposes. Ignoring these QC checks, as a commenter suggested, is inconsistent with EPA's NPDES permit requirements. Thus, 40 CFR 122.41(e) of EPA's NPDES permitting regulations provides that the permittee ''shall at all times properly operate and maintain all facilities and systems of treatment and control * * * Proper operation and maintenance also includes adequate laboratory controls and appropriate quality assurance procedures * * *.'' In most cases, these procedures are already a part of the quality control practices of most laboratories and will not create an additional burden. However, in codifying QC requirements, EPA provides clarification that these procedures are mandatory, as applicable, and not merely optional.

V. 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 today's 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. Although EPA expects that in some cases the analytical costs could increase slightly due to additional QC requirements for a few old EPA-approved methods that lack QA/QC, EPA has determined that most laboratories that analyze samples for EPA compliance monitoring have already instituted QC requirements as part of their laboratory practices and this rule will not have a significant economic impact on a substantial number of small entities.

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, today's 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 EO 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 EO has the potential to influence the regulation. This action is not subject to EO 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 is not adding two of the proposed ASTM methods to this final rule because these methods have not undergone full inter-laboratory validation as recommended in current Agency guidance (see Section III.C of this preamble). All other proposed voluntary consensus standards are approved in today's rule.

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

Executive Order (EO) 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 June 18, 2012.

List of Subjects

40 CFR Part 136

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

40 CFR Part 260

Environmental protection, Administrative practice and procedure, Confidential business information, Hazardous waste, Incorporation by reference, Reporting and recordkeeping requirements.

40 CFR Part 423

Environmental protection, Steam Electric Power Generating Point Source Category, Incorporation by reference, Reporting and recordkeeping requirements, Water pollution control.

40 CFR Part 430

Environmental protection, Pulp, Paper, and Paperboard Point Source Category, Incorporation by reference, Reporting and recordkeeping requirements, Water pollution control.

40 CFR Part 435

Environmental protection, Oil and Gas Extraction Point Source Category, Incorporation by reference, Reporting and recordkeeping requirements, Water pollution control.

Dated: April 17, 2012.

Lisa P. Jackson,

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 Administrator, or to a State having an approved NPDES program for a permit under section 402 of the Clean Water Act of 1977, as amended (CWA), and/or to reports required to be submitted under NPDES permits or other requests for quantitative or qualitative effluent data under parts 122 to 125 of title 40; 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 CWA, as amended.

* * * * *

■ 3. Section 136.3 is amended:

■ a. By revising paragraph (a) introductory text and Tables IA, IB, IC, ID, IG, and IH;

■ b. By revising paragraph (b);

■ c. By revising paragraph (e) introductory text;

■ d. By revising Table II to paragraph (e).

These 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. 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, 625, 1613, 1624, and 1625. The full texts of Methods 601–613, 624, 625, 1613, 1624, and 1625 are printed in appendix A of this part 136, and the full text of Method 200.7 is printed in appendix C of this part 136. The full text for determining the method detection limit when using the test procedures is given in appendix B of this part 136. The full text of Method 200.7 is printed in appendix C of this part 136. 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 text of the referenced test procedures are incorporated by reference into Tables IA, IB, IC, ID, IE, IF, IG, and IH. 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, § 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	p. 132 [3] .... 1680 [11,15]. 1681 [11,20].	9221 C E–2006.		
	Membrane filter (MF) [2], single step	p. 124 [3]	9222 D–1997	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.		
	MF [2], single step [5]	p. 124 [3]	9222 D–1997.		
3. Coliform (total), number per 100 mL.	MPN, 5 tube, 3 dilution, or.	p. 114 [3]	9221 B–2006.		
	MF [2], single step or two step.	p. 108 [3]	9222 B–1997	B–0025–85 [4]	
4. Coliform (total), in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or	p. 114 [3]	9221 B–2006		
	MF [2] with enrichment [5]	p. 111 [3]	9222 (B + B.5c) – 1997		
5. *E. coli,* number per 100 mL [21].	MPN [6,8,16] multiple tube, or.	....	9221B.1–2006/9221F–2006 [12,14].		
	multiple tube/multiple well, or	....	9223 B–2004 [13]	991.15 [10]	Colilert®[13,18] Colilert-18®[13,17,18]
	MF [2,6,7,8] single step ...	1603 [22]	....	....	mColiBlue-24®[19]
6. Fecal streptococci, number per 100 mL.	MPN, 5 tube 3 dilution, or	p. 139 [3]	9230 B–2007.		
	MF [2], or	p. 136 [3]	9230 C–2007	B–0055–85 [4]	
	Plate count	p. 143 [3].			
7. Enterococci, number per 100 mL [22].	MPN [6,8], multiple tube/ multiple well, or	....	....	D6503–99 [9]	Enterolert®[13,24]
	MF [2,6,7,8] single step or	1600 [25]	9230 C–2007		
	Plate count	p. 143 [3].			
8. *Salmonella,* number per gram dry weight [11].	MPN multiple tube	1682 [23].			
Aquatic Toxicity:					
9. Toxicity, acute, fresh water organisms, LC_{50}, percent effluent.	*Ceriodaphnia dubia* acute.	2002.0.[26]			
	Daphnia puplex and *Daphnia magna* acute.	2021.0.[26]			
	Fathead Minnow, *Pimephales promelas,* and Bannerfin shiner, *Cyprinella leedsi,* acute.	2000.0.[26]			
	Rainbow Trout, *Oncorhynchus mykiss,* and brook trout, *Salvelinus fontinalis,* acute.	2019.0.[26]			
10. Toxicity, acute, estuarine and marine organisms of the Atlantic Ocean and Gulf of Mexico, LC_{50}, percent effluent.	Mysid, *Mysidopsis bahia,* acute.	2007.0.[26]			

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
	Sheepshead Minnow, *Cyprinodon variegatus,* acute.	2004.0[26]			
	Silverside, *Menidia beryllina, Menidia menidia,* and *Menidia peninsulae,* acute.	2006.0[26]			
11. Toxicity, chronic, fresh water organisms, NOEC or IC_{25}, percent effluent.	Fathead minnow, *Pimephales promelas,* larval survival and growth.	1000.0.[27]			
	Fathead minnow, *Pimephales promelas,* embryo-larval survival and teratogenicity.	1001.0.[27]			
	Daphnia, *Ceriodaphnia dubia,* survival and reproduction.	1002.0.[27]			
	Green alga, *Selenastrum capricornutum,* growth.	1003.0.[27]			
12. Toxicity, chronic, estuarine and marine organisms of the Atlantic Ocean and Gulf of Mexico, NOEC or IC_{25}, percent effluent.	Sheepshead minnow, *Cyprinodon variegatus,* larval survival and growth.	1004.0.[28]			
	Sheepshead minnow, *Cyprinodon variegatus,* embryo-larval survival and teratogenicity.	1005.0.[28]			
	Inland silverside, *Menidia beryllina,* larval survival and growth.	1006.0.[28]			
	Mysid, *Mysidopsis bahia,* survival, growth, and fecundity.	1007.0.[28]			
	Sea urchin, *Arbacia punctulata,* 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. US 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] Recommended for enumeration of target organism in sewage sludge.

[12] The multiple-tube fermentation test is used in 9221B.1–2006. 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.1–2006, 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–10–003. April 2010. 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®, Quanti-Tray®/2000, 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®, Quanti-Tray®, and Quanti-Tray®/2000 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] Recommended 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–09–007. December 2009. U.S. EPA.

[23] Method 1682: *Salmonella* in Sewage Sludge (Biosolids) by Modified Semisolid Rappaport-Vassiliadis (MSRV) Medium, EPA–821–R–06–014. July 2006. 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–09–016. December 2009. 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.

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–1997	D1067–06	I–1020–85.[2]
2. Alkalinity, as $CaCO_3$, mg/L.	Electrometric or Colorimetric titration to pH 4.5, Manual.		2320 B–1997	D1067–06	973.43 [3], I–1030–85.[2]
	Automatic	310.2 (Rev. 1974)[1]			I–2030–85.[2]
3. Aluminum—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration [36]		3111 D–1999 or 3111 E–1999.		I–3051–85.[2]
	AA furnace		3113 B–2004.		
	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–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	Direct Current Plasma (DCP) [36].			D4190–08	See footnote.[34]
	Colorimetric (Eriochrome cyanine R).		3500–Al B–2001.		
4. Ammonia (as N), mg/L.	Manual distillation [6] or gas diffusion (pH > 11), followed by any of the following:	350.1, Rev. 2.0 (1993).	4500–NH_3 B–1997		973.49[3].
	Nesslerization			D1426–08 (A)	973.49[3], I–3520–85.[2]
	Titration		4500–NH_3 C–1997.		
	Electrode		4500–NH_3 D–1997 or E–1997.	D1426–08 (B).	
	Manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.		4500–NH_3 F–1997		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–1997 4500–NH_3 H–1997.		I–4523–85.[2]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Automated electrode	Ion Chromatography	....	D6919–09	See footnote.[7]
5. Antimony—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration [36].	....	3111 B–1999.		
	AA furnace	....	3113 B–2004.		
	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–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
6. Arsenic–Total,[4] mg/L.	Digestion,[4] followed by any of the following:	206.5 (Issued 1978) [1].			
	AA gaseous hydride	....	3114 B–2009 or 3114 C–2009	D2972–08 (B)	I–3062–85.[2]
	AA furnace	....	3113 B–2004	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–1999	D1976–07.	
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4020–05.[70]
	Colorimetric (SDDC)	....	3500–As B–1997	D2972–08 (A)	I–3060–85.[2]
7. Barium–Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration [36].	....	3111 D–1999	....	I–3084–85.[2]
	AA furnace	....	3113 B–2004	D4382–02(07).	
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	....	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP [36]	....	....	....	See footnote.[34]
8. Beryllium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration	....	3111 D–1999 or 3111 E–1999	D3645–08 (A)	I–3095–85.[2]
	AA furnace	....	3113 B–2004	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–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP	....	....	D4190–08	See footnote.[34]
	Colorimetric (aluminon).	....	See footnote [61].		
9. Biochemical oxygen demand (BOD5), mg/L.	Dissolved Oxygen Depletion.	....	5210 B–2001	....	973.44[3], p. 17.[9], I–1578–78,[8] See footnote.[10,63]
10. Boron—Total,[37] mg/L.	Colorimetric (curcumin) ..	....	4500–B B –2000	....	I–3112–85.[2]
	ICP/AES	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP	....	....	D4190–08	See footnote.[34]
11. Bromide, mg/L	Electrode	....	....	D1246–05	I–1125–85.[2]
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000, C–2000, D–2000.	D4327–03	993.30.[3]
	CIE/UV	....	4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
12. Cadmium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	AA direct aspiration [36].		3111 B–1999 or 3111 C–1999	D3557–02(07) (A or B).	974.27,[3] p. 37.[9], I–3135–85 [2] or I–3136–85.[2]
	AA furnace		3113 B–2004	D3557–02(07) (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–1999	D1976–07	I–1472–85 [2] or I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP[36]			D4190–08	See footnote.[34]
	Voltametry[11]			D3557–02(07) (C).	
	Colorimetric (Dithizone).		3500–Cd-D–1990.		
13. Calcium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration		3111 B–1999	D511–08(B)	I–3152–85.[2]
	ICP/AES	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999		I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
	DCP				See footnote.[34]
	Titrimetric (EDTA)		3500–Ca B–1997	D511–08 (A).	
	Ion Chromatography			D6919–09.	
14. Carbonaceous biochemical oxygen demand ($CBOD_5$), mg/L[12].	Dissolved Oxygen Depletion with nitrification inhibitor.		5210 B–2001		See footnote.[35,63]
15. Chemical oxygen demand (COD), mg/L.	Titrimetric	410.3 (Rev. 1978)[1]	5220 B–1997 or C–1997	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–1997	D1252–06 (B)	See footnotes.[13,14] I–3561–85.[2]
16. Chloride, mg/L	Titrimetric: (silver nitrate)		4500–Cl^- B–1997	D512–04 (B)	I–1183–85.[2]
	(Mercuric nitrate)		4500–Cl^- C–1997	D512–04 (A)	973.51,[3] I–1184–85.[2]
	Colorimetric: manual				I–1187–85.[2]
	Automated (Ferricyanide)		4500–Cl^- E–1997		I–2187–85.[2]
	Potentiometric Titration		4500–Cl^- D–1997.		
	Ion Selective Electrode			D512–04 (C).	
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or 4110 C–2000	D4327–03	993.30[3] , I–2057–90.[51]
	CIE/UV		4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
17. Chlorine–Total residual, mg/L.	Amperometric direct		4500–Cl D–2000	D1253–08.	
	Amperometric direct (low level).		4500–Cl E–2000.		
	Iodometric direct		4500–Cl B–2000.		
	Back titration ether end–point[15].		4500–Cl C–2000.		
	DPD–FAS		4500–Cl F–2000.		
	Spectrophotometric, DPD		4500–Cl G–2000.		
	Electrode				See footnote.[16]
17A. Chlorine–Free Available, mg/L.	Amperometric direct		4500–Cl D–2000	D1253–08.	
	Amperometric direct (low level).		4500–Cl E–2000.		
	DPD–FAS		4500–Cl F–2000.		
	Spectrophotometric, DPD		4500–Cl G–2000.		
18. Chromium VI dissolved, mg/L.	0.45-micron Filtration followed by any of the following:				
	AA chelation–extraction.		3111 C–1999		I–1232–85.[2]
	Ion Chromatography	218.6, Rev. 3.3 (1994).	3500–Cr C–2009	D5257–03	993.23.
	Colorimetric (Diphenyl–carbazide).		3500–Cr B–2009	D1687–02(07) (A)	I–1230–85.[2]
19. Chromium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	AA direct aspiration [36].		3111 B–1999	D1687–02(07) (B)	974.27,[3] I–3236–85.[2]
	AA chelation–extraction.		3111 C–1999.		
	AA furnace		3113 B–2004	D1687–02(07) (C)	I–3233–93.[46]
	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–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4020–05.[70]
	DCP [36]			D4190–08	See footnote.[34]
	Colorimetric (Diphenyl–carbazide).		3500–Cr B–2009.		
20. Cobalt—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration		3111 B–1999 or 3111 C–1999.	D3558–08 (A or B)	p. 37,[9] I–3239–85.[2]
	AA furnace		3113 B–2004	D3558–08 (C)	I–4243–89.[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–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4020–05.[70]
	DCP			D4190–08	See footnote.[34]
21. Color, platinum cobalt units or dominant wavelength, hue, luminance purity.	Colorimetric (ADMI)				See footnote.[18]
	(Platinum cobalt) Spectrophotometric.		2120 B–2001		I–1250–85.[2]
22. Copper—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration [36].		3111 B–1999 or 3111 C–1999	D1688–07 (A or B)	974.27,[3] p. 37,[9] I–3270–85 [2] or I–3271–85.[2]
	AA furnace		3113 B–2004	D1688–07 (C)	I–4274–89.[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–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4020–05.[70]
	DCP [36]			D4190–08	See footnote.[34]
	Colorimetric (Neocuproine).		3500–Cu B–1999.		
	(Bathocuproine)		3500–Cu C–1999		See footnote.[19]
23. Cyanide—Total, mg/L.	Automated UV digestion/distillation and Colorimetry.				Kelada–01.[55]
	Segmented Flow Injection, In-Line Ultraviolet Digestion, followed by gas diffusion amperometry.			D7511–09.	
	Manual distillation with $MgCl_2$, followed by any of the following:	335.4, Rev. 1.0 (1993) [57].	4500–CN^- B–1999 or C–1999.	D2036–09(A), D7284–08.	10–204–00–1–X.[56]
	Flow Injection, gas diffusion amperometry.			D2036–09(A) D7284–08.	
	Titrimetric		4500–CN^- D–1999	D2036–09(A)	p. 22.[9]
	Spectrophotometric, manual.		4500–CN^- E–1999	D2036–09(A)	I–3300–85.[2]
	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).	

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Ion Selective Electrode.	....	4500–CN$^-$ F–1999	D2036–09(A).	
24. Cyanide–Available, mg/L.	Cyanide Amenable to Chlorination (CATC); Manual distillation with $MgCl_2$, followed by Titrimetric or Spectrophotometric.	....	4500–CN$^-$ G–1999	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–1997.		
	Electrode, manual ...	....	4500–F$^-$ C–1997	D1179–04 (B).	
	Electrode, automated.	....	....	....	I–4327–85.[2]
	Colorimetric, (SPADNS).	....	4500–F$^-$ D–1997	D1179–04 (A).	
	Automated complexone.	....	4500–F$^-$ E–1997.		
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30.[3]
	CIE/UV	....	4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
26. Gold—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration	....	3111 B–1999.		
	AA furnace	231.2 (Issued 1978)[1]	3113 B–2004.		
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
	DCP	....	....	....	See footnote.[34]
27. Hardness—Total, as $CaCO_3$, mg/L.	Automated colorimetric ...	130.1 (Issued 1971)[1].			
	Titrimetric (EDTA)	....	2340 C–1997	D1126–02(07)	973.52B,[3] I–1338–85.[2]
	Ca plus Mg as their carbonates, by inductively coupled plasma or AA direct aspiration. (See Parameters 13 and 33)..	....	2340 B–1997.		
28. Hydrogen ion (pH), pH units.	Electrometric measurement.	....	4500–H$^+$ B–2000	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–1999.		
	AA furnace	235.2 (Issued 1978)[1].			
	ICP/MS	....	3125 B–2009.		
30. Iron—Total,[4] mg/L	Digestion,[4] followed by any of the following:				
	AA direct aspiration [36].	....	3111 B–1999 or 3111 C–1999	D1068–05 (A or B) ..	974.27,[3] I–3381–85.[2]
	AA furnace	....	3113 B–2004	D1068–05 (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–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	DCP [36]			D4190–08	See footnote.[34]
	Colorimetric (Phenanthroline).		3500-Fe-1997	D1068–05 (D)	See footnote.[22]
31. Kjeldahl Nitrogen [5]—Total, (as N), mg/L.	Manual digestion [20] and distillation or gas diffusion, followed by any of the following:		4500–N_{org} B–1997 or C–1997 and 4500–NH_3 B–1997.	D3590–02(06) (A)	I–4515–91.[45]
	Titration		4500–NH_3 C–1997		973.48.[3]
	Nesslerization			D1426–08 (A).	
	Electrode		4500–NH_3 D–1997 or E–1997.	D1426–08 (B).	
	Semi-automated phenate.	350.1 Rev 2.0 1993	4500–NH_3 G–1997. 4500–NH_3 H–1997.		
	Manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.		4500–NH_3 F–1997		See footnote.[60]
	Automated Methods for TKN that do not require manual distillation				
	Automated phenate, salicylate, or other substituted phenols in Berthelot reaction based methods colorimetric (auto digestion and distillation).	351.1 (Rev. 1978)[1]			I–4551–78.[8]
	Semi-automated block digestor colorimetric (distillation not required).	351.2, Rev. 2.0 (1993).	4500–N_{org} D–1997	D3590–02(06) (B)	I–4515–91.[45]
	Block digester, followed by Auto distillation and Titration.				See footnote.[39]
	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]
32. Lead—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration [36].		3111 B–1999 or 3111 C–1999.	D3559–08 (A or B)	974.27,[3] I–3399–85.[2]
	AA furnace		3113 B–2004	D3559–08 (D)	I–4403–89.[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–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP [36]			D4190–08	See footnote.[34]
	Voltametry[11]			D3559–08 (C).	
	Colorimetric (Dithizone).		3500–Pb B–1997.		
33. Magnesium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration		3111 B–1999	D511–08 (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–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
	DCP				See footnote.[34]
	Gravimetric.				
	Ion Chromatography			D6919–09.	
34. Manganese—Total,[4] mg/L.	Digestion [4] followed by any of the following:				

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	AA direct aspiration [36].		3111 B–1999	D858–07 (A or B)	974.27,[3] I–3454–85.[2]
	AA furnace		3113 B–2004	D858–07 (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–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP [36]			D4190–08	See footnote.[34]
	Colorimetric (Persulfate).		3500–Mn B–1999		920.203.[3]
	(Periodate)				See footnote.[23]
35. Mercury—Total,[4] mg/L.	Cold vapor, Manual	245.1, Rev. 3.0 (1994).	3112 B–2009	D3223–02(07)	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].			
36. Molybdenum—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration		3111 D–1999		I–3490–85.[2]
	AA furnace		3113 B–2004		I–3492–96.[47]
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP				See footnote.[34]
37. Nickel—Total,[4] mg/L.	Digestion [4] followed by any of the following:				
	AA direct aspiration [36].		3111 B–1999 or 3111 C–1999	D1886–08 (A or B)	I–3499–85.[2]
	AA furnace		3113 B–2004	D1886–08 (C)	I–4503–89.[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–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4020–05.[70]
	DCP [36]			D4190–08	See footnote.[34]
38. Nitrate (as N), mg/L.	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30.[3]
	CIE/UV		4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
	Ion Selective Electrode.		4500–NO_3^- D–2000.		
	Colorimetric (Brucine sulfate).	352.1 (Issued 1971)[1]			973.50,[3] 419D[1,7], p. 28.[9]
	Nitrate-nitrite N minus Nitrite N (See parameters 39 and 40).				See footnote.[62]
39. Nitrate-nitrite (as N), mg/L.	Cadmium reduction, Manual.		4500–NO_3^- E–2000	D3867–04 (B).	
	Cadmium reduction, Automated.	353.2, Rev. 2.0 (1993).	4500–NO_3^- F–2000	D3867–04 (A)	I–2545–90.[51]
	Automated hydrazine.		4500–NO_3^- H–2000.		
	Reduction/Colorimetric.				See footnote.[62]
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30.[3]
	CIE/UV		4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
40. Nitrite (as N), mg/L	Spectrophotometric: Manual.		4500–NO_2^- B–2000		See footnote.[25]
	Automated (Diazotization).				I–4540–85[2], See footnote.[62]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Automated (*bypass cadmium reduction).	353.2, Rev. 2.0 (1993).	4500–NO_3^- F–2000	D3867–04 (A)	I–4545–85.[2]
	Manual (*bypass cadmium reduction).		4500–NO_3^- E–2000	D3867–04 (B).	
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30.[3]
	CIE/UV		4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
41. Oil and grease—Total recoverable, mg/L.	Hexane extractable material (HEM): n–Hexane extraction and gravimetry.	1664 Rev. A; 1664 Rev. B[42].	5520 B–2001[38].		
	Silica gel treated HEM (SGT–HEM): Silica gel treatment and gravimetry.	1664 Rev. A; 1664 Rev. B[42].	5520 B–2001[38] and 5520 F–2001[38].		
42. Organic carbon—Total (TOC), mg/L.	Combustion		5310 B–2000	D7573–09	973.47[3], p. 14.[24]
	Heated persulfate or UV persulfate oxidation.		5310 C 2000 5310 D 2000.	D4839–03	973.47[3], p. 14.[24]
43. Organic nitrogen (as N), mg/L.	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–1999 or G–1999.		973.56[3], I–4601–85.[2]
	Manual single reagent.		4500–P E–1999	D515–88(A)	973.55.[3]
	Manual two reagent	365.3 (Issued 1978)[1].			
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30.[3]
	CIE/UV		4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
45. Osmium—Total[4], mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration,		3111 D–1999.		
	AA furnace	252.2 (Issued 1978)[1].			
46. Oxygen, dissolved, mg/L.	Winkler (Azide modification).		4500–O B–2001, C–2001, D–2001, E–2001, F–2001.	D888–09 (A)	973.45B[3], I–1575–78.[8]
	Electrode		4500–O G–2001	D888–09 (B)	I–1576–78.[8]
	Luminescence Based Sensor.			D888–09 (C)	See footnote[63] See footnote.[64]
47. Palladium—Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration		3111 B–1999.		
	AA furnace	253.2[1](Issued 1978).			
	ICP/MS		3125 B–2009.		
	DCP				See footnote.[34]
48. Phenols, mg/L	Manual distillation[26], followed by any of the following:	420.1[1](Rev. 1978)	5530 B–2005	D1783–01.	
	Colorimetric (4AAP) manual.	420.1[1](Rev. 1978)	5530 D–2005[27]	D1783–01 (A or B).	
	Automated colorimetric (4AAP).	420.4 Rev. 1.0 (1993).			
49. Phosphorus (elemental), mg/L.	Gas–liquid chromatography.				See footnote.[28]
50. Phosphorus—Total, mg/L.	Digestion[20], followed by any of the following:		4500–P B(5)-1999		973.55.[3]
	Manual	365.3[1](Issued 1978)	4500–P E–1999	D515–88 (A).	
	Automated ascorbic acid reduction.	365.1 Rev. 2.0 (1993).	4500–P F–1999, G–1999, H–1999.		973.56[3], I–4600–85.[2]
	ICP/AES[4, 36]	200.7, Rev. 4.4 (1994).	3120 B–1999		I–4471–97.[50]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Semi–automated block digestor (TKP digestion).	365.4[1] (Issued 1974)		D515–88 (B)	I–4610–91.[48]
51. Platinum—Total,[4] mg/L.	Digestion[4] followed by any of the following:				
	AA direct aspiration		3111 B–1999.		
	AA furnace	255.2 (Issued 1978)[1].			
	ICP/MS		3125 B–2009.		
	DCP				See footnote.[34]
52. Potassium—Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration		3111 B–1999		973.53[3], I–3630–85.[2]
	ICP/AES	200.7, Rev. 4.4 (1994).	3120 B–1999.		
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
	Flame photometric		3500–K B–1997.		
	Electrode		3500–K C–1997.		
	Ion Chromatography			D6919–09.	
53. Residue—Total, mg/L.	Gravimetric, 103–105°		2540 B–1997		I–3750–85.[2]
54. Residue—filterable, mg/L.	Gravimetric, 180°		2540 C–1997	D5907–03	I–1750–85.[2]
55. Residue—non–filterable (TSS), mg/L.	Gravimetric, 103–105° post washing of residue.		2540 D–1997	D5907–03	I–3765–85.[2]
56. Residue—settleable, mg/L.	Volumetric, (Imhoff cone), or gravimetric.		2540 F–1997.		
57. Residue—Volatile, mg/L.	Gravimetric, 550°	160.4 (Issued 1971)[1]	2540–E–1997		I–3753–85.[2]
58. Rhodium—Total,[4] mg/L.	Digestion[4] followed by any of the following:				
	AA direct aspiration, or.		3111 B–1999.		
	AA furnace	265.2 (Issued 1978)[1].			
	ICP/MS		3125 B–2009.		
59. Ruthenium—Total,[4] mg/L.	Digestion[4] followed by any of the following:				
	AA direct aspiration, or.		3111 B–1999.		
	AA furnace	267.2[1].			
	ICP/MS		3125 B–2009.		
60. Selenium—Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA furnace		3113 B–2004	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–1999	D1976–07.	
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14[3], I–4020–05.[70]
	AA gaseous hydride		3114 B–2009, or 3111 C–2009.	D3859–08 (A)	I–3667–85.[2]
61. Silica—Dissolved,[37] mg/L.	0.45-micron filtration followed by any of the following:				
	Colorimetric, Manual		4500–SiO_2 C–1997	D859–05	I–1700–85.[2]
	Automated (Molybdosilicate).		4500–SiO_2 E–1997 or F–1997.		I–2700–85.[2]
	ICP/AES	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999		I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
62. Silver—Total,[4, 31] mg/L.	Digestion[4, 29], followed by any of the following:				
	AA direct aspiration		3111 B–1999 or 3111 C–1999		974.27[3], p. 37[9], I–3720–85.[2]
	AA furnace		3113 B–2004		I–4724–89.[51]
	STGFAA	200.9, Rev. 2.2 (1994).			

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	ICP/AES	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14[3], I–4471–97.[50]
	DCP				See footnote.[34]
63. Sodium—Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration		3111 B–1999		973.54[3], I–3735–85.[2]
	ICP/AES	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999		I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
	DCP				See footnote.[34]
	Flame photometric		3500–Na B–1997.		
	Ion Chromatography			D6919–09.	
64. Specific conductance, micromhos/cm at 25°C.	Wheatstone bridge	120.1[1](Rev. 1982)	2510 B–1997	D1125–95(99) (A)	973.40[3], I–2781–85.[2]
65. Sulfate (as SO_4), mg/L.	Automated colorimetric	375.2, Rev. 2.0 (1993).	4500–SO_4^{2} F–1997 or G–1997.		
	Gravimetric		4500–SO_4^{2} C–1997 or D–1997.		925.54.[3]
	Turbidimetric		4500–SO_4^{2} E–1997.	D516–07.	
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30[3], I–4020–05.[70]
	CIE/UV		4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
66. Sulfide (as S), mg/L.	Sample Pretreatment		4500–S^{2-} B, C–2000.		
	Titrimetric (iodine)		4500–S^{2-}F–2000		I–3840–85.[2]
	Colorimetric (methylene blue).		4500–S^{2-}D–2000.		
	Ion Selective Electrode.		4500–S^{2-}G–2000	D4658–08.	
67. Sulfite (as SO_3), mg/L.	Titrimetric (iodine-iodate)		4500–SO_3^{2-}B–2000.		
68. Surfactants, mg/L	Colorimetric (methylene blue).		5540 C–2000	D2330–02.	
69. Temperature, °C	Thermometric		2550 B–2000		See footnote.[32]
70. Thallium–Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration		3111 B–1999.		
	AA furnace	279.2[1](Issued 1978)	3113 B–2004.		
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES	200.7, Rev. 4.4 (1994); 200.5 Rev. 4.2 (2003)[68].	3120 B–1999	D1976–07.	
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14[3], I–4471–97.[50]
71. Tin–Total,[4] mg/L	Digestion[4], followed by any of the following:.				
	AA direct aspiration		3111 B–1999		I–3850–78.[8]
	AA furnace		3113 B–2004.		
	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–2009	D5673–05	993.14.[3]
72. Titanium–Total,[4] mg/L.	Digestion[4] followed by any of the following:				
	AA direct aspiration		3111 D–1999.		
	AA furnace	283.2[1](Issued 1978).			
	ICP/AES	200.7, Rev. 4.4 (1994).			
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	DCP				See footnote.[34]
73. Turbidity, NTU[53]	Nephelometric	180.1, Rev. 2.0 (1993).	2130 B–2001	D1889–00	I–3860–85.[2] See footnote.[65] See footnote.[66] See footnote.[67]
74. Vanadium–Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration		3111 D–1999.		
	AA furnace		3113 B–2004	D3373–03(07).	
	ICP/AES	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14[3], I–4020–05.[70]
	DCP			D4190–08	See footnote.[34]
	Colorimetric (Gallic Acid).		3500–V B–1997.		
75. Zinc–Total[4], mg/L	Digestion[4], followed by any of the following:				
	AA direct aspiration[36].		3111 B–1999 or 3111 C–1999.	D1691–02(07) (A or B).	974.27[3], p. 37[9], I–3900–85.[2]
	AA furnace	289.2[1](Issued 1978).			
	ICP/AES[36]	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14[3], I–4020–05.[70]
	DCP[36]			D4190–08	See footnote.[34]
	Colorimetric (Zincon)		3500 Zn B–1997		See footnote.[33]
76. 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 the 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 ($CBOD_5$) must not be confused with the traditional BOD_5 test method which measures "total BOD." The addition of the nitrification inhibitor is not a procedural option, but must be included to report the $CBOD_5$ parameter. A discharger whose permit requires reporting the traditional BOD_5 may not use a nitrification inhibitor in the procedure for reporting the results. Only when a discharger's permit specifically states $CBOD_5$ 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, December 1971.

[19] Method 8506, Biocinchoninate 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) p. 14. 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 $Na_2S_2O_3$ 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 NH_4OH, 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 NH_4OH. 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, 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 300.1–1, 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, Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte. December 2000. Waters Corp.

[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 aluminon 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 BOD_5 and $cBOD_5$. 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.

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, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98)	
2. Acenaphthylene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
3. Acrolein	GC	603.			
	GC/MS	624 [4], 1624B.			
4. Acrylonitrile	GC	603.			
	GC/MS	624 [4], 1624B.			
5. Anthracene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440B–2000	D4657–92 (98).	
6. Benzene	GC	602	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
7. Benzidine	Spectro-photo-metric.				See footnote [3], p.1.
	GC/MS	625 [5], 1625B	6410 B–2000.		
	HPLC	605.			
8. Benzo(a)anthracene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
9. Benzo(a)pyrene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
10. Benzo(b)fluoranthene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
11. Benzo(g,h,i)perylene	GC	610.			

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

Parameter [1]	Method	EPA [2,7]	Standard methods	ASTM	Other
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
12. Benzo(k)fluoranthene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	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, 1625B	6410 B–2000		See footnote [9], p. 27.
15. bis(2-Chloroethoxy) methane	GC	611.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
16. bis(2-Chloroethyl) ether	GC	611.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
17. bis(2-Ethylhexyl) phthalate	GC	606.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
18. Bromodichloromethane	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
19. Bromoform	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
20. Bromomethane	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
21. 4-Bromophenyl phenyl ether	GC	611.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
22. Carbon tetrachloride	GC	601	6200 C–1997		See footnote [3], p. 130.
	GC/MS	624, 1624B	6200 B–1997.		
23. 4-Chloro-3-methyl phenol	GC	604	6420 B–2000.		
	GC/MS	625, 1625B	6410 B–2000.		See footnote [9], p. 27.
24. Chlorobenzene	GC	601, 602	6200 C–1997		See footnote [3], p. 130.
	GC/MS	624, 1624B	6200 B–1997.		
25. Chloroethane	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
26. 2-Chloroethylvinyl ether	GC	601.			
	GC/MS	624, 1624B.			
27. Chloroform	GC	601	6200 C–1997		See footnote [3], p. 130.
	GC/MS	624, 1624B	6200 B–1997.		
28. Chloromethane	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
29. 2-Chloronaphthalene	GC	612.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
30. 2-Chlorophenol	GC	604	6420 B–2000.		
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
31. 4-Chlorophenyl phenyl ether	GC	611.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
32. Chrysene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
33. Dibenzo(a,h)anthracene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
34. Dibromochloromethane	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
35. 1,2-Dichlorobenzene	GC	601, 602	6200 C–1997.		

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

Parameter [1]	Method	EPA [2,7]	Standard methods	ASTM	Other
	GC/MS	624, 1625B	6200 B–1997		See footnote [9], p. 27.
36. 1,3-Dichlorobenzene	GC	601, 602	6200 C–1997.		
	GC/MS	624, 1625B	6200 B–1997		See footnote [9], p. 27.
37. 1,4-Dichlorobenzene	GC	601, 602	6200 C–1997.		
	GC/MS	624, 1625B	6200 B–1997		See footnote [9], p. 27.
38. 3,3'-Dichlorobenzidine	GC/MS	625, 1625B	6410 B–2000.		
	HPLC	605.			
39. Dichlorodifluoromethane	GC	601.			
	GC/MS		6200 C–1997.		
40. 1,1-Dichloroethane	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
41. 1,2-Dichloroethane	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
42. 1,1-Dichloroethene	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
43. trans-1,2-Dichloroethene	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
44. 2,4-Dichlorophenol	GC	604	6420 B–2000.		
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
45. 1,2-Dichloropropane	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
46. cis-1,3-Dichloropropene	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
47. trans-1,3-Dichloropropene	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
48. Diethyl phthalate	GC	606.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
49. 2,4-Dimethylphenol	GC	604	6420 B–2000.		
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
50. Dimethyl phthalate	GC	606.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
51. Di-n-butyl phthalate	GC	606.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
52. Di-n-octyl phthalate	GC	606.			
	GC/MS	625, 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, 1625B	6410 B–2000.		
54. 2,4-Dinitrotoluene	GC	609.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
55. 2,6-Dinitrotoluene	GC	609.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
56. Epichlorohydrin	GC				See footnote [3], p. 130.
	GC/MS				See footnote [6], p. S102.
57. Ethylbenzene	GC	602	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
58. Fluoranthene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
59. Fluorene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	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-p-dioxin	GC/MS	1613B.			
63. Hexachlorobenzene	GC	612.			

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

Parameter [1]	Method	EPA [2,7]	Standard methods	ASTM	Other
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
64. Hexachlorobutadiene	GC	612.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
65. Hexachlorocyclopentadiene	GC	612.			
	GC/MS	625 [5], 1625B	6410 B–2000		See footnote [9], p. 27.
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-p-dioxin	GC/MS	1613B.			
71. 1,2,3,6,7,8-Hexachloro-dibenzo-p-dioxin	GC/MS	1613B.			
72. 1,2,3,7,8,9-Hexachloro-dibenzo-p-dioxin	GC/MS	1613B.			
73. Hexachloroethane	GC	612.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
74. Indeno(1,2,3-c,d) pyrene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
75. Isophorone	GC	609.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
76. Methylene chloride	GC	601	6200 C–1997.		See footnote [3], p. 130.
	GC/MS	624, 1624B	6200 B–1997.		
77. 2-Methyl-4,6-dinitrophenol	GC	604	6420 B–2000.		
	GC/MS	625, 1625B	6410 B–2000.		See footnote [9], p. 27.
78. Naphthalene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000.		See footnote [9], p. 27
	HPLC	610	6440 B–2000.		
79. Nitrobenzene	GC	609.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC			D4657–92 (98).	
80. 2-Nitrophenol	GC	604	6420 B–2000.		
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
81. 4-Nitrophenol	GC	604	6420 B–2000.		
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
82. N-Nitrosodimethylamine	GC	607.			
	GC/MS	625 [5], 1625B	6410 B–2000		See footnote [9], p. 27.
83. N-Nitrosodi-n-propylamine	GC	607.			
	GC/MS	625 [5], 1625B	6410 B–2000		See footnote [9], p. 27.
84. N-Nitrosodiphenylamine	GC	607.			
	GC/MS	625 [5], 1625B	6410 B–2000		See footnote [9], p. 27.
85. Octachlorodibenzofuran	GC/MS	1613B.[10]			
86. Octachlorodibenzo-p-dioxin	GC/MS	1613B.[10]			
87. 2,2'-Oxybis(2-chloro-propane) [also known as bis(2-Chloroisopropyl) ether].	GC	611.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
88. PCB–1016	GC	608			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625	6410 B–2000.		
89. PCB–1221	GC	608			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625	6410 B–2000.		
90. PCB–1232	GC	608			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
	GC/MS	625	6410 B–2000.		
91. PCB–1242	GC	608			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625	6410 B–2000.		
92. PCB–1248	GC	608.			
	GC/MS	625	6410 B–2000.		
93. PCB–1254	GC	608			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625	6410 B–2000.		
94. PCB–1260	GC	608			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625	6410 B–2000.		
95. 1,2,3,7,8-Pentachloro-dibenzofuran	GC/MS	1613B.			
96. 2,3,4,7,8-Pentachloro-dibenzofuran	GC/MS	1613B.			
97. 1,2,3,7,8,-Pentachloro-dibenzo-p-dioxin	GC/MS	1613B.			
98. Pentachlorophenol	GC	604	6420 B–2000		See footnote [3], p. 140.
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
99. Phenanthrene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
100. Phenol	GC	604	6420 B–2000.		
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
101. Pyrene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
102. 2,3,7,8-Tetrachloro-dibenzofuran	GC/MS	1613B.[10]			
103. 2,3,7,8-Tetrachloro-dibenzo-p-dioxin	GC/MS	613, 625 [5a], 1613B.			
104. 1,1,2,2-Tetrachloroethane	GC	601	6200 C–1997		See footnote [3], p. 130.
	GC/MS	624, 1624B	6200 B–1997.		
105. Tetrachloroethene	GC	601	6200 C–1997		See footnote [3], p. 130.
	GC/MS	624, 1624B	6200 B–1997.		
106. Toluene	GC	602	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
107. 1,2,4-Trichlorobenzene	GC	612			See footnote [3], p. 130.
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
108. 1,1,1-Trichloroethane	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
109. 1,1,2-Trichloroethane	GC	601	6200 C–1997.		See footnote [3], p. 130.
	GC/MS	624, 1624B	6200 B–1997.		
110. Trichloroethene	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
111. Trichlorofluoromethane	GC	601	6200 C–1997.		
	GC/MS	624	6200 B–1997.		
112. 2,4,6-Trichlorophenol	GC	604	6420 B–2000.		
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
113. Vinyl chloride	GC	601	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
114. Nonylphenol	GC/MS			D7065–06.	
115. Bisphenol A (BPA)	GC/MS			D7065–06.	
116. p-tert-Octylphenol (OP)	GC/MS			D7065–06.	
117. Nonylphenol Monoethoxylate (NP1EO)	GC/MS			D7065–06.	
118. Nonylphenol Diethoxylate (NP2EO)	GC/MS			D7065–06.	
119. Adsorbable Organic Halides (AOX)	Adsorption and Coulometric Titration.	1650.[11]			

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

Parameter [1]	Method	EPA [2,7]	Standard methods	ASTM	Other
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, 624, 625, 1613B, 1624B, and 1625B are provided at Appendix A, Test Procedures for Analysis of Organic Pollutants, of this Part 136. The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, of this Part 136.

[3] Methods for Benzidine: Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater. September 1978. U.S. EPA.

[4] Method 624 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.

[5] Method 625 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, 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, 624, 625, 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 and 625 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 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–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 40 CFR Part 136 and at *http://water.epa.gov/scitech/methods/cwa/index.cfm*

[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, The Pulp, Paper, and Paperboard Point Source Category.

TABLE ID—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES [1]

Parameter	Method	EPA [2,7,10]	Standard methods	ASTM	Other
1. Aldrin	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96 (02).	See footnote [3], p. 7; See footnote [4], O–3104–83; See footnote [8], 3M0222.
	GC/MS	625	6410 B–2000.		
2. Ametryn	GC	507, 619			See footnote [3], p. 83; See footnote [9], O–3106–93; See footnote [6], p. S68.
	GC/MS	525.2			See footnote [14], O–1121–91.
3. Aminocarb	TLC				See footnote [3], p. 94; See footnote [6], p. S60.
	HPLC	632.			
4. Atraton	GC	619			See footnote [3], p. 83; See footnote [6], p. S68.
5. Atrazine	GC	507, 619			See footnote [3], p. 83; See footnote [6], p. S68; See footnote [9], O–3106–93.
	HPLC/MS				See footnote [12], O–2060–01.
	GC/MS	525.1, 525.2			See footnote [11], O–1126–95.
6. Azinphos methyl	GC	614, 622, 1657			See footnote [3], p. 25; See footnote [6], p. S51.
	GC-MS				See footnote [11], O–1126–95.
7. Barban	TLC				See footnote [3], p. 104; See footnote [6], p. S64.
	HPLC	632.			
8. α-BHC	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7; See footnote [8], 3M0222.
	GC/MS	625 [5]	6410 B–2000		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
9. β–BHC	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [8], 3M0222.
	GC/MS	625	6410 B–2000.		
10. δ-BHC	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [8], 3M0222.
	GC/MS	625	6410 B–2000.		
11. γ-BHC (Lindane)	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7; See footnote [4], O–3104–83; See footnote [8], 3M0222.
	GC/MS	625 [5]	6410 B–2000		See footnote [11], O–1126–95.
12. Captan	GC	617	6630 B–2000	D3086–90, D5812–96(02).	See footnote [3], p. 7.
13. Carbaryl	TLC				See footnote [3], p. 94, See footnote [6], p. S60.
	HPLC	531.1, 632.			
	HPLC/MS	553			See footnote [12], O–2060–01.
	GC/MS				See footnote [11], O–1126–95.
14. Carbophenothion	GC	617	6630 B–2000		See footnote [4], page 27; See footnote [6], p. S73.
15. Chlordane	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7; See footnote [4], O–3104–83; See footnote [8], 3M0222.
	GC/MS	625	6410 B–2000.		
16. Chloropropham	TLC				See footnote [3], p. 104; See footnote [6], p. S64.
	HPLC	632.			
17. 2,4-D	GC	615	6640 B–2001		See footnote [3], p. 115; See footnote [4], O–3105 –83.
	HPLC/MS				See footnote [12], O–2060–01.
18. 4,4'-DDD	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7; See footnote [4], O–3105–83; See footnote [8], 3M0222.
	GC/MS	625	6410 B–2000.		
19. 4,4'-DDE	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7; See footnote [4], O–3104–83; See footnote [8], 3M0222.
	GC/MS	625	6410 B–2000		See footnote [11], O–1126–95.
20. 4,4'-DDT	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7; See footnote [4], O–3104–83; See footnote [8], 3M0222.
	GC/MS	625	6410 B–2000.		
21. Demeton-O	GC	614, 622			See footnote [3], p. 25; See footnote [6], p. S51.
22. Demeton-S	GC	614, 622			See footnote [3], p. 25; See footnote [6], p. S51.
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			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	6630 B–2000		See footnote [3], p. 7;
27. Dicofol	GC	617			See footnote [4], O–3104–83.
28. Dieldrin	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7; See footnote [4], O–3104–83; See footnote [8], 3M0222.
	GC/MS	625	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			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.

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

Parameter	Method	EPA [2,7,10]	Standard methods	ASTM	Other
32. Endosulfan I	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7; See footnote [4], O–3104–83; See footnote [8], 3M022).
	GC/MS	625 [5]	6410 B–2000		See footnote [13], O–2002–01.
33. Endosulfan II	GC	608, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7; See footnote [8], 3M0222.
	GC/MS	625 [5]	6410 B–2000		See footnote [13], O–2002–01.
34. Endosulfan Sulfate	GC	608, 617	6630 C–2000		See footnote [8], 3M0222.
	GC/MS	625	6410 B–2000		
35. Endrin	GC	505, 508, 608, 617, 1656	6630 B–2000 & C–2000.	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 [5]	6410 B–2000.		
36. Endrin aldehyde	GC	608, 617	6630 C–2000		See footnote [8], 3M0222.
	GC/MS	625.			
37. Ethion	GC	614, 614.1,1657			See footnote [4], page 27; See footnote [6], p. S73.
	GC/MS				See footnote [13], O–2002–01.
38. Fenuron	TLC				See footnote [3], p. 104; See footnote [6], p. S64.
	HPLC	632.			
	HPLC/MS				See footnote [12], O–2060–01.
39. Fenuron-TCA	TLC				See footnote [3], p. 104; See footnote [6], p. S64.
	HPLC	632.			
40. Heptachlor	GC	505, 508, 608, 617, 1656	6630 B–2000 & C–2000.	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	6410 B–2000.		
41. Heptachlor epoxide	GC	608, 617	6630 B–2000 & C–2000.	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	6410 B–2000.		
42. Isodrin	GC	617	6630 B–2000 & C–2000.		See footnote [4], O–3104–83; See footnote [6], p. S73.
43. Linuron	GC				See footnote [3], p. 104; See footnote [6], p. S64.
	HPLC	632.			
	HPLC/MS	553			See footnote [12], O–2060–01.
	GC/MS				See footnote [11], O–1126–95.
44. Malathion	GC	614, 1657	6630 B–2000		See footnote [3], p. 25; See footnote [6], p. S51.
	GC/MS				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.	6630 B–2000 & C–2000.	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			See footnote [11], O–1126–95.
47. Mexacarbate	TLC				See footnote [3], p. 94; See footnote [6], p.S60.
	HPLC	632.			
48. Mirex	GC	617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7; See footnote [4], O–3104–83.
49. Monuron	TLC				See footnote [3], p. 104; See footnote [6], p. S64.
	HPLC	632.			
50. Monuron-TCA	TLC				See footnote [3], p. 104; See footnote [6], p. S64.
	HPLC	632.			
51. Neburon	TLC				See footnote [3], p. 104; See footnote [6], p. S64.
	HPLC	632.			
	HPLC/MS				See footnote [12], O–2060–01.
52. Parathion methyl	GC	614, 622, 1657	6630 B–2000		See footnote [4], page 27; See footnote [3], p. 25.

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

Parameter	Method	EPA [2,7,10]	Standard methods	ASTM	Other
	GC/MS				See footnote [11], O–1126–95.
53. Parathion ethyl	GC	614	6630 B–2000		See footnote [4], page 27; See footnote [3], p. 25.
	GC/MS				See footnote [11], O–1126–95.
54. PCNB	GC	608.1, 617	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7.
55. Perthane	GC	617		D3086–90, D5812–96(02).	See footnote [4], O–3104–83.
56. Prometon	GC	507, 619			See footnote [3], p. 83; See footnote [6], p. S68; See footnote [9], O–3106–93.
	GC/MS	525.2			See footnote [11], O–1126–95.
57. Prometryn	GC	507, 619			See footnote [3], p. 83; See footnote [6], p. S68; See footnote [9],O–3106–93.
	GC/MS	525.1, 525.2			See footnote [13], O–2002–01.
58. Propazine	GC	507, 619, 1656			See footnote [3], p. 83; See footnote [6], p. S68; See footnote [9], O–3106–93.
	GC/MS	525.1, 525.2.			
59. Propham	TLC				See footnote [3], p. 104; See footnote [6], p. S64.
	HPLC	632.			
	HPLC/MS				See footnote [12], O–2060–01.
60. Propoxur	TLC				See footnote [3], p. 94; See footnote [6], p. S60.
	HPLC	632.			
61. Secbumeton	TLC				See footnote [3], p. 83; See footnote [6], p. S68.
	GC	619.			
62. Siduron	TLC				See footnote [3], p. 104; See footnote [6], p. S64.
	HPLC	632.			
	HPLC/MS				See footnote [12], O–2060–01.
63. Simazine	GC	505, 507, 619, 1656			See footnote [3], p. 83; See footnote [6], p. S68; See footnote [9], O–3106–93.
	GC/MS	525.1, 525.2			See footnote [11], O–1126–95.
64. Strobane	GC	617	6630 B–2000 & C–2000.		See footnote [3], p. 7.
65. Swep	TLC				See footnote [3], p. 104; See footnote [6], p. S64.
	HPLC	632.			
66. 2,4,5-T	GC	615	6640 B–2001		See footnote [3], p. 115; See footnote [4], O–3105–83.
67. 2,4,5-TP (Silvex)	GC	615	6640 B–2001		See footnote [3], p. 115; See footnote [4], O–3105–83.
68. Terbuthylazine	GC	619, 1656			See footnote [3], p. 83; See footnote [6], p. S68.
	GC/MS				See footnote [13], O–2002–01.
69. Toxaphene	GC	505, 508, 608, 617, 1656	6630 B–2000 & C–2000.	D3086–90, D5812–96(02).	See footnote [3], p. 7; See footnote [8]; See footnote [4], O–3105–83.
	GC/MS	525.1, 525.2, 625	6410 B–2000.		
70. Trifluralin	GC	508, 617, 627, 1656	6630 B–2000		See footnote [3], p. 7; See footnote [9], O–3106–93.
	GC/MS	525.2			See footnote [11], O–1126–95.

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, 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, Definition and Procedure for the Determination of the Method Detection Limit, of this Part 136.

[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 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 and 625 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 10% of all samples analyzed with Method 608 or 5% of all samples analyzed with Method 625 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. The full text of Methods 608 and 625 are provided at Appendix A, Test Procedures for Analysis of Organic Pollutants, of this Part 136. 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.

[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.

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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
12	Dichlorvos	62–73–7	1657/507/622/525.1/525.2
16	2,4-D; 2,4-D Salts and Esters [2,4-Dichloro-phenoxyacetic 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
25	Cyanazine	21725–46–2	629/507
26	Propachlor	1918–16–7	1656/508/608.1/525.1/525.2
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
41	Propanil	709–98–8	632.1/1656
45	Metribuzin	21087–64–9	507/633/525.1/525.2/1656
52	Acephate	30560–19–1	1656/1657
53	Acifluorfen	50594–66–6	515.1/515.2/555
54	Alachlor	15972–60–8	505/507/645/525.1/525.2/1656
55	Aldicarb	116–06–3	531.1
58	Ametryn	834–12–8	507/619/525.2
60	Atrazine	1912–24–9	505/507/619/525.1/525.2/1656
62	Benomyl	17804–35–2	631
68	Bromacil; Bromacil Salts and Esters	314–40–9	507/633/525.1/525.2/1656
69	Bromoxynil	1689–84–5	1625/1661
69	Bromoxynil octanoate	1689–99–2	1656
70	Butachlor	23184–66–9	507/645/525.1/525.2/1656
73	Captafol	2425–06–1	1656
75	Carbaryl [Sevin]	63–25–2	531.1/632/553
76	Carbofuran	1563–66–2	531.1/632
80	Chloroneb	2675–77–6	1656/508/608.1/525.1/525.2
82	Chlorothalonil	1897–45–6	508/608.2/525.1/525.2/1656
84	Stirofos	961–11–5	1657/507/622/525.1/525.2
86	Chlorpyrifos	2921–88–2	1657/508/622
90	Fenvalerate	51630–58–1	1660
103	Diazinon	333–41–5	1657/507/614/622/525.2
107	Parathion methyl	298–00–0	1657/614/622
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

TABLE IG—TEST METHODS FOR PESTICIDE ACTIVE INGREDIENTS (40 CFR PART 455)—Continued

EPA survey code	Pesticide name	CAS No.	EPA analytical method No.(s) [3]
112	Dinoseb	88–85–7	1658/515.1/615/515.2/555
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	1656/505/508/608/617/525.1/525.2
125	Ethalfluralin	55283–68–6	1656/627 See footnote 1
126	Ethion	563–12–2	1657/614/614.1
127	Ethoprop	13194–48–4	1657/507/622/525.1/525.2
132	Fenarimol	60168–88–9	507/633.1/525.1/525.2/1656
133	Fenthion	55–38–9	1657/622
138	Glyphosate [N-(Phosphonomethyl) glycine]	1071–83–6	547
140	Heptachlor	76–44–8	1656/505/508/608/617/525.1/525.2
144	Isopropalin	33820–53–0	1656/627
148	Linuron	330–55–2	553/632
150	Malathion	121–75–5	1657/614
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
172	Nabam	142–59–6	630/630.1
173	Naled	300–76–5	1657/622
175	Norflurazon	27314–13–2	507/645/525.1/525.2/1656
178	Benfluralin	1861–40–1	1656/627 See footnote 1
182	Fensulfothion	115–90–2	1657/622
183	Disulfoton	298–04–4	1657/507/614/622/525.2
185	Phosmet	732–11–6	1657/622.1
186	Azinphos Methyl	86–50–0	1657/614/622
192	Organo-tin pesticides	12379–54–3	Ind-01/200.7/200.9
197	Bolstar	35400–43–2	1657/622
203	Parathion	56–38–2	1657/614
204	Pendimethalin	40487–42–1	1656
205	Pentachloronitrobenzene	82–68–8	1656/608.1/617
206	Pentachlorophenol	87–86–5	625/1625/515.2/555/515.1/525.1/525.2
208	Permethrin	52645–53–1	608.2/508/525.1/525.2/1656/1660
212	Phorate	298–02–2	1657/622
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
224	Prometryn	7287–19–6	507/619/525.1/525.2
226	Propazine	139–40–2	507/619/525.1/525.2/1656
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
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
254	Terbacil	5902–51–2	507/633/525.1/525.2/1656
255	Terbufos	13071–79–9	1657/507/614.1/525.1/525.2
256	Terbuthylazine	5915–41–3	619/1656
257	Terbutryn	886–50–0	507/619/525.1/525.2
259	Dazomet	533–74–4	630/630.1/1659
262	Toxaphene	8001–35–2	1656/505/508/608/617/525.1/525.2
263	Merphos [Tributyl phosphorotrithioate]	150–50–5	1657/507/525.1/525.2/622
264	Trifluralin [1]	1582–09–8	1656/508/617/627/525.2
268	Ziram [Zinc dimethyldithiocarbamate]	137–30–4	630/630.1

Table 1G 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, 625 and 1625 are provided at Appendix A of this Part 136. The full text of Method 200.7 is provided at Appendix C of this Part 136.

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.	p. 132 [3]	9221 C E–2006.		
	Membrane filter (MF) [2], single step.	p. 124 [3]	9222 D–1997	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.		
	MF [2], single step [5]	p. 124 [3]	9222 D–1997.		
3. Coliform (total), number per 100 mL.	MPN, 5 tube, 3 dilution, or.	p. 114 [3]	9221 B–2006.		
	MF [2], single step or two step.	p. 108 [3]	9222 B–1997	B–0025–85 [4]	
4. Coliform (total), in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or.	p. 114 [3]	9221 B–2006.		
	MF [2] with enrichment	p. 111 [3]	9222 (B+B.5c)–1997.		
5. *E. coli,* number per 100 mL.	MPN [6,8,14], multiple tube, or.		9221 B.1–2006/9221 F–2006 [11,13].		
	Multiple tube/multiple well, or.		9223 B–2004 [12]	991.15 [10]	Colilert®[12,16], Colilert-18®[12,15,16].
	MF [2,5,6,7,8], two step, or	1103.1 [19]	9222 B–1997/9222 G–1997 [18], 9213 D–2007.	D5392–93 [9].	
	Single step	1603 [20], 1604 [21].			mColiBlue-24®[17].
6. Fecal streptococci, number per 100 mL.	MPN, 5 tube, 3 dilution, or.	p. 139 [3]	9230 B–2007.		
	MF [2], or	p. 136 [3]	9230 C–2007	B–0055–85 [4].	
	Plate count	p. 143 [3].			
7. Enterococci, number per 100 mL.	MPN [6,8], multiple tube/multiple well, or.			D6503–99 [9]	Enterolert®[12,22].
	MF [2,5,6,7,8] two step, or	1106.1 [23]	9230 C–2007	D5259–92 [9].	
	Single step, or	1600 [24]	9230 C–2007.		
	Plate count	p. 143 [3].			
Protozoa:					
8. *Cryptosporidium*	Filtration/IMS/FA	1622 [25], 1623 [26].			
9. *Giardia*	Filtration/IMS/FA	1623 [26]			

Table 1H 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. US 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.1–2006. 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.1–2006, 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®, Quanti-Tray®, and Quanti-Tray®/2000 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–1997 or other membrane filter procedure to 9222G–1997 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. US 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–09–007. December 2009. US 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, US 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. US EPA.

[24] Method 1600: Enterococci in Water by Membrane Filtration Using membrane-Enterococcus Indoxyl-β-D-Glucoside Agar (mEI), EPA–821–R–09–016. December 2009. US 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. US 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. US EPA.

(b) The documents required in this section are incorporated by reference into this section with approval of the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies of the documents may be obtained from the sources listed in paragraph (b) of this section. Documents may be inspected at EPA's Water Docket, EPA West, 1301 Constitution Avenue NW., Room B102, Washington, DC (Telephone: 202–566–2426); or 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: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html.* These test procedures are incorporated as they exist on the day of approval and a notice of any change in these test procedures will be published in the **Federal Register**. The full texts of the methods from the following references which are cited in Tables IA, IB, IC, ID, IE, IF, IG and IH are incorporated by reference into this regulation and may be obtained from the source identified. All costs cited are subject to change and must be verified from the indicated source.

(1) Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati OH (US EPA). Available at *http://water.epa.gov/scitech/methods/cwa/index.cfm* or from: National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161

(i) Microbiological Methods for Monitoring the Environment, Water, and Wastes. 1978. EPA/600/8–78/017, Pub. No. PB–290329/A.S.

(A) Part III Analytical Methodology, Section B Total Coliform Methods, page 108. Table IA, Note 3; Table IH, Note 3.

(B) Part III Analytical Methodology, Section B Total Coliform Methods, 2.6.2 Two-Step Enrichment Procedure, page 111. Table IA, Note 3; Table IH, Note 3.

(C) Part III Analytical Methodology, Section B Total Coliform Methods, 4 Most Probable Number (MPN) Method, page 114. Table IA, Note 3; Table IH, Note 3.

(D) Part III Analytical Methodology, Section C Fecal Coliform Methods, 2 Direct Membrane Filter (MF) Method, page 124. Table IA, Note 3; Table IH, Note 3.

(E) Part III, Analytical Methodology, Section C Fecal Coliform Methods, 5 Most Probable Number (MPN) Method, page 132. Table IA, Note 3; Table IH, Note 3.

(F) Part III Analytical Methodology, Section D Fecal Streptococci, 2 Membrane Filter (MF) Method, page 136. Table IA, Note 3; Table IH, Note 3.

(G) Part III Analytical Methodology, Section D Fecal Streptococci, 4 Most Probable Number Method, page 139. Table IA, Note 3; Table IH, Note 3.

(H) Part III Analytical Methodology, Section D Fecal Streptococci, 5 Pour Plate Method, page 143. Table IA, Note 3; Table IH, Note 3.

(ii) [Reserved]

(2) Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati OH (US EPA). Available at *http://water.epa.gov/scitech/methods/cwa/index.cfm.*

(i) Method 300.1 (including Errata Cover Sheet, April 27, 1999), Determination of Inorganic Ions in Drinking Water by Ion Chromatography, Revision 1.0, 1997. Table IB, Note 52.

(ii) Method 551, Determination of Chlorination Disinfection Byproducts and Chlorinated Solvents in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography With Electron-Capture Detection. 1990. Table IF.

(3) National Exposure Risk Laboratory-Cincinnati, U.S. Environmental Protection Agency, Cincinnati OH (US EPA). Available from *http://water.epa.gov/scitech/methods/cwa/index.cfm* or from the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161. Telephone: 800–553–6847.

(i) Methods for the Determination of Inorganic Substances in Environmental Samples. August 1993. EPA/600/R–93/100, Pub. No. PB 94120821. Table IB, Note 52.

(A) Method 180.1, Determination of Turbidity by Nephelometry. Revision 2.0. Table IB, Note 52.

(B) Method 300.0, Determination of Inorganic Anions by Ion Chromatography. Revision 2.1. Table IB, Note 52.

(C) Method 335.4, Determination of Total Cyanide by Semi-Automated Colorimetry. Revision 1.0. Table IB, Notes 52 and 57.

(D) Method 350.1, Determination of Ammonium Nitrogen by Semi-Automated Colorimetry. Revision 2.0. Table IB, Notes 30 and 52.

(E) Method 351.2, Determination of Total Kjeldahl Nitrogen by Semi-Automated Colorimetry. Revision 2.0. Table IB, Note 52.

(F) Method 353.2, Determination of Nitrate-Nitrite Automated Colorimetry. Revision 2.0. Table IB, Note 52.

(G) Method 365.1, Determination of Phosphorus by Automated Colorimetry. Revision 2.0. Table IB, Note 52.

(H) Method 375.2, Determination of Sulfate by Automated Colorimetry. Revision 2.0. Table IB, Note 52.

(I) Method 410.4, Determination of Chemical Oxygen Demand by Semi-Automated Colorimetry. Revision 2.0. Table IB, Note 52.

(ii) Methods for the Determination of Metals in Environmental Samples, Supplement I. May 1994. EPA/600/R–94/111, Pub. No. PB 95125472. Table IB, Note 52.

(A) Method 200.7, Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry. Revision 4.4. Table IB, Note 52.

(B) Method 200.8, Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma Mass Spectrometry. Revision 5.3. Table IB, Note 52.

(C) Method 200.9, Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry. Revision 2.2. Table IB, Note 52.

(D) Method 218.6, Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography. Revision 3.3. Table IB, Note 52.

(E) Method 245.1, Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry. Revision 3.0. Table IB, Note 52.

(4) National Exposure Risk Laboratory-Cincinnati, U.S. Environmental Protection Agency, Cincinnati OH (US EPA). Available at *http://water.epa.gov/scitech/methods/cwa/index.cfm*.

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

(ii) EPA Method 525.2, Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry. Revision 2.0, 1995. Table ID, Note 10.

(5) Office of Research and Development, Cincinnati OH. U.S. Environmental Protection Agency, Cincinnati OH (US EPA). Available at *http://water.epa.gov/scitech/methods/cwa/index.cfm* or from ORD Publications, CERI, U.S. Environmental Protection Agency, Cincinnati OH 45268.

(i) Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol, and Pesticides in Water and Wastewater. 1978. Table IC, Note 3; Table ID, Note 3.

(ii) Methods for Chemical Analysis of Water and Wastes. March 1979. EPA–600/4–79–020. Table IB, Note 1.

(iii) Methods for Chemical Analysis of Water and Wastes. Revised March 1983. EPA–600/4–79–020. Table IB, Note 1.

(A) Method 120.1, Conductance, Specific Conductance, μmhos at 25 °C. Revision 1982. Table IB, Note 1.

(B) Method 130.1, Hardness, Total (mg/L as $CaCO_3$), Colorimetric, Automated EDTA. Issued 1971. Table IB, Note 1.

(C) Method 150.2, pH, Continuous Monitoring (Electrometric). December 1982. Table IB, Note 1.

(D) Method 160.4, Residue, Volatile, Gravimetric, Ignition at 550 °C. Issued 1971. Table IB, Note 1.

(E) Method 206.5, Arsenic, Sample Digestion Prior to Total Arsenic Analysis by Silver Diethyldithiocarbamate or Hydride Procedures. Issued 1978. Table IB, Note 1.

(F) Method 231.2, Gold, Atomic Absorption, Furnace Technique. Issued 1978. Table IB, Note 1.

(G) Method 245.2, Mercury, Automated Cold Vapor Technique. Issued 1974. Table IB, Note 1.

(H) Method 252.2, Osmium, Atomic Absorption, Furnace Technique. Issued 1978. Table IB, Note 1.

(I) Method 253.2, Palladium, Atomic Absorption, Furnace Technique. Issued 1978. Table IB, Note 1.

(J) Method 255.2, Platinum, Atomic Absorption, Furnace Technique. Issued 1978. Table IB, Note 1.

(K) Method 265.2, Rhodium, Atomic Absorption, Furnace Technique. Issued 1978. Table IB, Note 1.

(L) Method 279.2, Thallium, Atomic Absorption, Furnace Technique. Issued 1978. Table IB, Note 1.

(M) Method 283.2, Titanium, Atomic Absorption, Furnace Technique. Issued 1978. Table IB, Note 1.

(N) Method 289.2, Zinc, Atomic Absorption, Furnace Technique. Issued 1978. Table IB, Note 1.

(O) Method 310.2, Alkalinity, Colorimetric, Automated, Methyl Orange. Revision 1974. Table IB, Note 1.

(P) Method 351.1, Nitrogen, Kjeldahl, Total, Colorimetric, Automated Phenate. Revision 1978. Table IB, Note 1.

(Q) Method 352.1, Nitrogen, Nitrate, Colorimetric, Brucine. Issued 1971. Table IB, Note 1.

(R) Method 365.3, Phosphorus, All Forms, Colorimetric, Ascorbic Acid, Two Reagent. Issued 1978. Table IB, Note 1.

(S) Method 365.4, Phosphorus, Total, Colorimetric, Automated, Block Digestor AA II. Issued 1974. Table IB, Note 1.

(T) Method 410.3, Chemical Oxygen Demand, Titrimetric, High Level for Saline Waters. Revision 1978. Table IB, Note 1.

(U) Method 420.1, Phenolics, Total Recoverable, Spectrophotometric, Manual 4–AAP With Distillation. Revision 1978. Table IB, Note 1.

(iv) Prescribed Procedures for Measurement of Radioactivity in Drinking Water. 1980. EPA–600/4–80–032. Table IE.

(A) Method 900.0, Gross Alpha and Gross Beta Radioactivity. Table IE.

(B) Method 903.0, Alpha-Emitting iRadio Isotopes. Table IE.

(C) Method 903.1, Radium-226, Radon Emanation Technique. Table IE.

(D) Appendix B, Error and Statistical Calculations. Table IE.

(6) Office of Science and Technology, U.S. Environmental Protection Agency, Washington DC (US EPA). Available at *http://water.epa.gov/scitech/methods/cwa/index.cfm*.

(i) Method 1625C, Semivolatile Organic Compounds by Isotope Dilution GCMS. 1989. Table IF.

(ii) [Reserved]

(7) Office of Water, U.S. Environmental Protection Agency, Washington DC (US EPA). Available at *http://water.epa.gov/scitech/methods/cwa/index.cfm* or from National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

(i) Method 1631, Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. Revision E, August 2002. EPA–821–R–02–019, Pub. No. PB2002–108220. Table IB, Note 43.

(ii) Kelada-01, Kelada Automated Test Methods for Total Cyanide, Acid Dissociable Cyanide, and Thiocyanate. Revision 1.2, August 2001. EPA 821–B–01–009, Pub. No. PB 2001–108275. Table IB, Note 55.

(iii) In the compendium *Analytical Methods for the Determination of Pollutants in Pharmaceutical Manufacturing Industry Wastewaters*. July 1998. EPA 821–B–98–016, Pub. No. PB95201679. Table IF, Note 1.

(A) EPA Method 1666, Volatile Organic Compounds Specific to the Pharmaceutical Industry by Isotope Dilution GC/MS. Table IF, Note 1.

(B) EPA Method 1667, Formaldehyde, Isobutyraldehyde, and Furfural by Derivatization Followed by High Performance Liquid Chromatography. Table IF.

(C) Method 1671, Volatile Organic Compounds Specific to the

Pharmaceutical Manufacturing Industry by GC/FID. Table IF.

(iv) Methods For The Determination of Nonconventional Pesticides In Municipal and Industrial Wastewater, Volume I. Revision I, August 1993. EPA 821–R–93–010A, Pub. No. PB 94121654. Tables ID, IG.

(A) Method 608.1, Organochlorine Pesticides. Table ID, Note 10; Table IG, Note 3.

(B) Method 608.2, Certain Organochlorine Pesticides. Table ID, Note 10; Table IG, Note 3.

(C) Method 614, Organophosphorus Pesticides. Table ID, Note 10; Table IG, Note 3.

(D) Method 614.1, Organophosphorus Pesticides. Table ID, Note 10; Table IG, Note 3.

(E) Method 615, Chlorinated Herbicides. Table ID, Note 10; Table IG, Note 3.

(F) Method 617, Organohalide Pesticides and PCBs. Table ID, Note 10; Table IG, Note 3.

(G) Method 619, Triazine Pesticides. Table ID, Note 10; Table IG, Note 3.

(H) Method 622, Organophosphorus Pesticides. Table ID, Note 10; Table IG, Note 3.

(I) Method 622.1, Thiophosphate Pesticides. Table ID, Note 10; Table IG, Note 3.

(J) Method 627, Dinitroaniline Pesticides. Table ID, Note 10; Table IG, Notes 1 and 3.

(K) Method 629, Cyanazine. Table IG, Note 3.

(L) Method 630, Dithiocarbamate Pesticides. Table IG, Note 3.

(M) Method 630.1, Dithiocarbamate Pesticides. Table IG, Note 3.

(N) Method 631, Benomyl and Carbendazim. Table IG, Note 3.

(O) Method 632, Carbamate and Urea Pesticides. Table ID, Note 10; Table IG, Note 3.

(P) Method 632.1, Carbamate and Amide Pesticides. Table IG, Note 3.

(Q) Method 633, Organonitrogen Pesticides. Table IG, Note 3.

(R) Method 633.1, Neutral Nitrogen-Containing Pesticides. Table IG, Note 3.

(S) Method 637, MBTS and TCMTB. Table IG, Note 3.

(T) Method 644, Picloram. Table IG, Note 3.

(U) Method 645, Certain Amine Pesticides and Lethane. Table IG, Note 3.

(V) Method 1656, Organohalide Pesticides. Table ID, Note 10; Table IG, Notes 1 and 3.

(W) Method 1657, Organophosphorus Pesticides. Table ID, Note 10; Table IG, Note 3.

(X) Method 1658, Phenoxy-Acid Herbicides. Table IG, Note 3.

(Y) Method 1659, Dazomet. Table IG, Note 3.

(Z) Method 1660, Pyrethrins and Pyrethroids. Table IG, Note 3.

(AA) Method 1661, Bromoxynil. Table IG, Note 3.

(BB) Ind-01. Methods EV–024 and EV–025, Analytical Procedures for Determining Total Tin and Triorganotin in Wastewater. Table IG, Note 3.

(v) Methods For The Determination of Nonconventional Pesticides In Municipal and Industrial Wastewater, Volume II. August 1993. EPA 821–R–93–010B, Pub. No. PB 94166311. Table IG.

(A) Method 200.9, Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry. Table IG, Note 3.

(B) Method 505, Analysis of Organohalide Pesticides and Commercial Polychlorinated Biphenyl (PCB) Products in Water by Microextraction and Gas Chromatography. Table ID, Note 10; Table IG, Note 3.

(C) Method 507, The Determination of Nitrogen- and Phosphorus-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus Detector. Table ID, Note 10; Table IG, Note 3.

(D) Method 508, Determination of Chlorinated Pesticides in Water by Gas Chromatography with an Electron Capture Detector. Table ID, Note 10; Table IG, Note 3.

(E) Method 515.1, Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector. Table IG, Notes 2 and 3.

(F) Method 515.2, Determination of Chlorinated Acids in Water Using Liquid-Solid Extraction and Gas Chromatography with an Electron Capture Detector. Table IG, Notes 2 and 3.

(G) Method 525.1, Determination of Organic Compounds in Drinking Water by Liquids-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry. Table ID, Note 10; Table IG, Note 3.

(H) Method 531.1, Measurement of N-Methylcarbamoyloximes and N-Methylcarbamates in Water by Direct Aqueous Injection HPLC with Post-Column Derivatization. Table ID, Note 10; Table IG, Note 3.

(I) Method 547, Determination of Glyphosate in Drinking Water by Direct-Aqueous-Injection HPLC, Post-Column Derivatization, and Fluorescence Detection. Table IG, Note 3.

(J) Method 548, Determination of Endothall in Drinking Water by Aqueous Derivatization, Liquid-Solid Extraction, and Gas Chromatography with Electron-Capture Detector. Table IG, Note 3.

(K) Method 548.1, Determination of Endothall in Drinking Water by Ion-Exchange Extraction, Acidic Methanol Methylation and Gas Chromatography/Mass Spectrometry. Table IG, Note 3.

(L) Method 553, Determination of Benzidines and Nitrogen-Containing Pesticides in Water by Liquid-Liquid Extraction or Liquid-Solid Extraction and Reverse Phase High Performance Liquid Chromatography/Particle Beam/Mass Spectrometry Table ID, Note 10; Table IG, Note 3.

(M) Method 555, Determination of Chlorinated Acids in Water by High Performance Liquid Chromatography With a Photodiode Array Ultraviolet Detector. Table IG, Note 3.

(vi) In the compendium *Methods for the Determination of Organic Compounds in Drinking Water.* Revised July 1991, December 1998. EPA–600/4–88–039, Pub. No. PB92–207703. Table IF.

(A) EPA Method 502.2, Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series. Table IF.

(B) [Reserved]

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(25) National Council of the Paper Industry for Air and Stream Improvements, Inc. (NCASI), 260 Madison Avenue, New York NY 10016.

(i) 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.

(ii) [Reserved]

(26) Oceanography International Corporation, 512 West Loop, P.O. Box 2980, College Station TX 77840.

(i) OIC Chemical Oxygen Demand Method. 1978. Table IB, Note 13.

(ii) [Reserved]

(27) OI Analytical, Box 9010, College Station TX 77820–9010.

(i) Method OIA–1677–09, Available Cyanide by Ligand Exchange and Flow Injection Analysis (FIA). Copyright 2010. Table IB, Note 59.

(ii) Method PAI–DK01, Nitrogen, Total Kjeldahl, Block Digestion, Steam Distillation, Titrimetric Detection. Revised December 22, 1994. Table IB, Note 39.

(iii) Method PAI–DK02, Nitrogen, Total Kjeldahl, Block Digestion, Steam Distillation, Colorimetric Detection. Revised December 22, 1994. Table IB, Note 40.

(iv) Method PAI–DK03, Nitrogen, Total Kjeldahl, Block Digestion, Automated FIA Gas Diffusion. Revised December 22, 1994. Table IB, Note 41.

(28) ORION Research Corporation, 840 Memorial Drive, Cambridge, Massachusetts 02138.

(i) ORION Research Instruction Manual, Residual Chlorine Electrode Model 97–70. 1977. Table IB, Note 16.

(ii) [Reserved]

(29) Technicon Industrial Systems, Tarrytown NY 10591.

(i) Industrial Method Number 379–75WE Ammonia, Automated Electrode Method, Technicon Auto Analyzer II. February 19, 1976. Table IB, Note 7.

(ii) [Reserved]

(30) Thermo Jarrell Ash Corporation, 27 Forge Parkway, Franklin MA 02038.

(i) Method AES0029. Direct Current Plasma (DCP) Optical Emission Spectrometric Method for Trace Elemental Analysis of Water and Wastes. 1986, Revised 1991. Table IB, Note 34.

(ii) [Reserved]

(31) Thermo Scientific, 166 Cummings Center, Beverly MA 01915. Telephone: 1–800–225–1480. *www.thermoscientific.com*.

(i) Thermo Scientific Orion Method AQ4500, Determination of Turbidity by Nephelometry. Revision 5, March 12, 2009. Table IB, Note 67.

(ii) [Reserved]

(32) 3M Corporation, 3M Center Building 220–9E–10, St. Paul MN 55144–1000.

(i) Organochlorine Pesticides and PCBs in Wastewater Using Empore™ Disk'' Test Method 3M 0222. Revised October 28, 1994. Table IC, Note 8; Table ID, Note 8.

(ii) [Reserved]

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

(ii) 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.

(iii) 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.

(iv) 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.

(v) 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.

(vi) 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.

(vii) 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.

(viii) 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.

(ix) 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.

(x) 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.

(xi) 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.

(xii) 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.

(xiii) 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.

(xiv) 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 Chormatography/Mass Spectrometry. 2001. Table ID, Note 12.

(xv) 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.

(xvi) 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.

(xvii) 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.

(xviii) 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.

(xix) 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.

(xx) 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.

(34) Waters Corporation, 34 Maple Street, Milford MA 01757, Telephone: 508–482–2131, Fax: 508–482–3625.

(i) Method D6508, Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte. Revision 2, December 2000. Table IB, Note 54.

(ii) [Reserved]

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(e) Sample preservation procedures, container materials, and maximum allowable holding times for parameters are cited in Tables IA, IB, IC, ID, IE, IF, IG, and IH are prescribed in Table II. Information in the table takes precedence over information in specific methods or elsewhere. Any person may apply for a change from the prescribed preservation techniques, container materials, and maximum holding times applicable to samples taken from a specific discharge. Applications for such limited use changes may be made by letters to the Regional Alternative Test Procedure (ATP) Program Coordinator or the permitting authority in the Region in which the discharge will occur. Sufficient data should be provided to assure such changes in sample preservation, containers or holding times do not adversely affect the integrity of the sample. The Regional ATP Coordinator or permitting authority will review the application and then notify the applicant and the appropriate State agency of approval or rejection of the use of the alternate test procedure. A decision to approve or deny any request on deviations from the prescribed Table II requirements will be made within 90 days of receipt of the application by the Regional Administrator. An analyst may not modify any sample preservation and/or holding time requirements of an approved method unless the requirements of this section are met.

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 *E. coli*	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$ [5].	8 hours.[22,23]
6. Fecal streptococci	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$ [5].	8 hours.[22]
7. Enterococci	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$ [5].	8 hours.[22]
8. *Salmonella*	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$ [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_2SO_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_2SO_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_2SO_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_2SO_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.
38. Nitrate	P, FP, G	Cool, ≤6 °C [18]	48 hours.
39. Nitrate-nitrite	P, FP, G	Cool, ≤6 °C[18], H_2SO_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_2SO_4 to pH <2.	28 days.
42. Organic Carbon	P, FP, G	Cool to ≤6 °C [18], HCl, H_2SO_4, or H_3PO_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_2SO_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_2SO_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.

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

Parameter number/name	Container [1]	Preservation [2,3]	Maximum holding time [4]
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.
73. Turbidity	P, FP, G	Cool, ≤6 °C [18]	48 hours.
Table IC—Organic Tests: [8]	.		
13, 18–20, 22, 24–28, 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% $Na_2S_2O_3$[5].	14 days.
6, 57, 106. Purgeable aromatic hydrocarbons	G, FP-lined septum	Cool, ≤6 °C[18], 0.008% $Na_2S_2O_3$ [5], HCl to pH 2 [9].	14 days.[9]
3, 4. Acrolein and acrylonitrile	G, FP-lined septum	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$, 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% $Na_2S_2O_3$.	7 days until extraction, 40 days after extraction.
7, 38. Benzidines [11,12]	G, FP-lined cap	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$[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% $Na_2S_2O_3$[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% $Na_2S_2O_3$[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% $Na_2S_2O_3$[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% $Na_2S_2O_3$[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].	.		
Aqueous Samples: Field and Lab Preservation	G	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$[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_2SO_4 to pH <2.	28 days until extraction, 40 days after extraction.
119. Adsorbable Organic Halides (AOX)	G	Cool, <6 °C, 0.008% $Na_2S_2O_3$ HNO_3 to pH <2.	Hold *at least* 3 days, but not more than 6 months.
120. Chlorinated Phenolics		Cool, <6 °C, 0.008% $Na_2S_2O_3$ H_2SO_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. *E. coli*	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$[5].	8 hours.[22]
2. Enterococci	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$ [5].	8 hours.[22]
Table IH—Protozoan Tests:	.		
8. *Cryptosporidium*	LDPE; field filtration	1–10 °C	96 hours.[21]
9. *Giardia*	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 sample (*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 141.34(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 (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) 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 has 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 Administrator under Sec. 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). Also, Section 9060A of Standard Methods for the Examination of Water and Wastewater (20th and 21st editions) addresses dechlorination procedures.

[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 ≤ 6 °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 °C.

[14] For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$ 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% $Na_2S_2O_3$.

[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 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 ≤ 6 °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 "≤ °C" is used in place of the "4 °C" and "< 4 °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 ≤6 °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).

■ 4. Section 136.4 is revised 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 alternate test procedure (ATP) under this paragraph (a) shall:

(1) Provide the name and address of the responsible person or firm making the application.

(2) Identify the pollutant(s) or parameter(s) for which nationwide approval of an alternate test procedure is being requested.

(3) Provide a detailed description of the proposed alternate test procedure, together with references to published or other studies confirming the general applicability of the alternate test procedure for the analysis of the pollutant(s) or parameter(s) in wastewater discharges from representative and specified industrial or other categories.

(4) Provide comparability data for the performance of the proposed alternative test procedure compared to the performance of the reference method.

(b) The National Coordinator may request additional information and analyses from the applicant in order to determine 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 acceptance or rejection of the alternate test procedure for nationwide use in CWA programs. If the application is not approved, the National Coordinator will specify what additional information might lead to a reconsideration of the application, and notify the Regional Alternate Test Procedure Coordinators of such rejection. Based on the National Coordinator's rejection of a proposed alternate test procedure and an assessment of any approvals for limited uses for the unapproved method, the Regional ATP Coordinator or permitting authority may decide to withdraw approval of the method for limited use in the Region.

(2) Where the National Coordinator approved an applicant's request for nationwide use of an alternate test procedure, the National Coordinator will notify the applicant that the National Coordinator will recommend rulemaking to approve the alternate test procedure. The National Coordinator will notify the Regional ATP Coordinator or permitting authorities 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 applicant's application. The Regional ATP Coordinator or permitting authority will grant approval on a case-by-case basis prior to use of the alternate test procedure for compliance analyses until the alternate test procedure is approved by publication in a final rule in the **Federal Register**.

(3) EPA will propose to amend 40 CFR Part 136 to include the alternate test procedure in § 136.3. EPA shall make available for review all the factual bases for its proposal, including 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 40 CFR Part 136 to include the alternate test procedure as an approved analytical method.

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

■ 5. Section 136.5 is revised to read as follows:

§ 136.5 Approval of alternate test procedures for limited use.

(a) Any person may request the Regional Alternate Test Procedure (ATP) Coordinator or permitting authority 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 or permitting authority with a recommendation for or against approval.

(c) Any application for approval of an alternate test procedure for limited use may be made by letter, email or by hard copy. The application shall include the following:

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

(2) Identify the pollutant or parameter for which approval of an alternate test procedure is being requested.

(3) Provide justification for using testing procedures other than those specified in Tables IA through IH of § 136.3, or in the NPDES permit.

(4) Provide a detailed description of the proposed alternate test procedure, together with references to published studies of the applicability of the alternate test procedure to the effluents in question.

(5) Provide comparability data for the performance of the proposed alternate test procedure compared to the performance of the reference method.

(d) *Approval for limited use.* (1) 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. 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 or permitting authority, to all discharger or facilities (and their associated laboratories) specified in the approval for the Region. If the application is not approved, the Regional ATP Coordinator or permitting authority shall specify what additional information might lead to a reconsideration of the application.

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

■ 6. Section 136.6 is revised to read as follows:

§ 136.6 Method modifications and analytical requirements.

(a) *Definitions of terms used in this section*—(1) *Analyst* means the person or laboratory using a test procedure (analytical method) in this Part.

(2) *Chemistry of the method* means the reagents and reactions used in a test procedure that allow determination of the analyte(s) of interest in an environmental sample.

(3) *Determinative technique* means the way in which an analyte is identified and quantified (*e.g.,* colorimetry, mass spectrometry).

(4) *Equivalent performance* means that the modified method produces results that meet or exceed the QC acceptance criteria of the approved method.

(5) *Method-defined analyte* means an analyte defined solely by the method used to determine the analyte. Such an analyte may be a physical parameter, a parameter that is not a specific chemical, or a parameter that may be comprised of a number of substances. Examples of such analytes include temperature, oil and grease, total suspended solids, total phenolics, turbidity, chemical oxygen demand, and biochemical oxygen demand.

(6) *QC* means ''quality control.''

(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. 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. The user 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 user may indicate the specific paragraph of § 136.6 allowing the method modification. However, specific details of the modification need not be provided, but must be documented in the Standard Operating Procedure (SOP). If the method user is uncertain whether a method modification is allowed, the Regional ATP Coordinator or permitting authority 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 be sufficiently sensitive and 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.

(i) *Requirements for establishing equivalent performance.* If the approved method contains QC tests and QC acceptance criteria, the modified method must use these QC tests and the modified method must meet the QC acceptance criteria with the following conditions:

(A) The analyst may only rely on QC tests and QC acceptance criteria in a method if it includes wastewater matrix QC tests and QC acceptance criteria (*e.g.,* matrix spikes) and both initial (start-up) and ongoing QC tests and QC acceptance criteria.

(B) If the approved method does not contain QC tests and QC acceptance criteria or if the QC tests and QC acceptance criteria in the method do not meet the requirements of this section, then the analyst must employ QC tests published in the ''equivalent'' of a Part 136 method that has such QC, or the essential QC requirements specified at 136.7, as applicable. If the approved method is from a compendium or VCSB and the QA/QC requirements are published in other parts of that organization's compendium rather than within the Part 136 method then that part of the organization's compendium must be used for the QC tests.

(C) In addition, the analyst must perform ongoing QC tests, including assessment of performance of the modified method on the sample matrix (*e.g.,* analysis of a matrix spike/matrix spike duplicate pair for every twenty samples), and analysis of an ongoing precision and recovery sample (*e.g.,* laboratory fortified blank or blank spike) and a blank with each batch of 20 or fewer samples.

(D) If the performance of the modified method in the wastewater matrix or reagent water does not meet or exceed the QC acceptance criteria, the method modification may not be used.

(ii) *Requirements for documentation.* The modified method must be documented in a method write-up or an addendum that describes the modification(s) to the approved method prior to the use of the method for compliance purposes. The write-up or addendum must include a reference number (*e.g.,* method number), revision number, and revision date so that it may be referenced accurately. In addition, the organization that uses the modified method must document the results of QC tests and keep these records, along with a copy of the method write-up or addendum, for review by an auditor.

(3) *Restrictions.* An analyst may not modify an approved Clean Water Act analytical method for a method-defined

analyte. In addition, an analyst may not modify an approved method if the modification would result in measurement of a different form or species of an analyte. Changes in method procedures are not allowed if such changes would alter the defined chemistry (*i.e.,* method principle) of the unmodified method. For example, phenol method 420.1 or 420.4 defines phenolics as ferric iron oxidized compounds that react with 4-aminoantipyrine (4-AAP) at pH 10 after being distilled from acid solution. Because total phenolics represents a group of compounds that all react at different efficiencies with 4-AAP, changing test conditions likely would change the behavior of these different phenolic compounds. An analyst may not modify any sample collection, preservation, or holding time requirements of an approved method. Such modifications to sample collection, preservation, and holding time requirements do not fall within the scope of the flexibility allowed at § 136.6. Method flexibility refers to modifications of the analytical procedures used for identification and measurement of the analyte only and does not apply to sample collection, preservation, or holding time procedures, which may only be modified as specified in § 136.3(e).

(4) *Allowable changes.* Except as noted under paragraph (b)(3) of this section, an analyst may modify an approved test procedure (analytical method) provided that the underlying reactions and principles used in the approved method remain essentially the same, and provided that the requirements of this section are met. If equal or better performance can be obtained with an alternative reagent, then it is allowed. A laboratory wishing to use these modifications must demonstrate acceptable method performance by performing and documenting all applicable initial demonstration of capability and ongoing QC tests and meeting all applicable QC acceptance criteria as described in § 136.7. Some examples of the allowed types of changes, provided the requirements of this section are met include:

(i) Changes between manual method, flow analyzer, and discrete instrumentation.

(ii) Changes in chromatographic columns or temperature programs.

(iii) Changes between automated and manual sample preparation, such as digestions, distillations, and extractions; in-line sample preparation is an acceptable form of automated sample preparation for CWA methods.

(iv) In general, ICP–MS is a sensitive and selective detector for metal analysis; however isobaric interference can cause problems for quantitative determination, as well as identification based on the isotope pattern. Interference reduction technologies, such as collision cells or reaction cells, are designed to reduce the effect of spectroscopic interferences that may bias results for the element of interest. The use of interference reduction technologies is allowed, provided the method performance specifications relevant to ICP–MS measurements are met.

(v) The use of EPA Method 200.2 or the sample preparation steps from EPA Method 1638, including the use of closed-vessel digestion, is allowed for EPA Method 200.8, provided the method performance specifications relevant to the ICP–MS are met.

(vi) Changes in pH adjustment reagents. Changes in compounds used to adjust pH are acceptable as long as they do not produce interference. For example, using a different acid to adjust pH in colorimetric methods.

(vii) Changes in buffer reagents are acceptable provided that the changes do not produce interferences.

(viii) Changes in the order of reagent addition are acceptable provided that the change does not alter the chemistry and does not produce an interference. For example, using the same reagents, but adding them in different order, or preparing them in combined or separate solutions (so they can be added separately), is allowed, provided reagent stability or method performance is equivalent or improved.

(ix) Changes in calibration range (provided that the modified range covers any relevant regulatory limit and the method performance specifications for calibration are met).

(x) Changes in calibration model. (A) Linear calibration models do not adequately fit calibration data with one or two inflection points. For example, vendor-supplied data acquisition and processing software on some instruments may provide quadratic fitting functions to handle such situations. If the calibration data for a particular analytical method routinely display quadratic character, using quadratic fitting functions may be acceptable. In such cases, the minimum number of calibrators for second order fits should be six, and in no case should concentrations be extrapolated for instrument responses that exceed that of the most concentrated calibrator. Examples of methods with nonlinear calibration functions include chloride by SM4500–Cl–E–1997, hardness by EPA Method 130.1, cyanide by ASTM D6888 or OIA1677, Kjeldahl nitrogen by PAI–DK03, and anions by EPA Method 300.0.

(B) As an alternative to using the average response factor, the quality of the calibration may be evaluated using the Relative Standard Error (RSE). The acceptance criterion for the RSE is the same as the acceptance criterion for Relative Standard Deviation (RSD), in the method. RSE is calculated as:

$$\%\,RSE = 100 \times \sqrt{\frac{\sum_{i=1}^{n}\left[\frac{x'_i - x_i}{x_i}\right]^2}{(n-p)}}$$

Where:

x'_i = Calculated concentration at level i

x_i = Actual concentration of the calibration level i

n = Number of calibration points

p = Number of terms in the fitting equation (average = 1, linear = 2, quadratic = 3)

(C) Using the RSE as a metric has the added advantage of allowing the same numerical standard to be applied to the calibration model, regardless of the form of the model. Thus, if a method states that the RSD should be ≤20% for the traditional linear model through the origin, then the RSE acceptance limit can remain ≤20% as well. Similarly, if a method provides an RSD acceptance limit of ≤15%, then that same figure can be used as the acceptance limit for the RSE. The RSE may be used as an alternative to correlation coefficients and coefficients of determination for evaluating calibration curves for any of the methods at Part 136. If the method includes a numerical criterion for the RSD, then the same numerical value is used for the RSE. Some older methods do not include any criterion for the calibration curve—for these methods, if RSE is used the value should be ≤20%. Note that the use of the RSE is included as an alternative to the use of the correlation coefficient as a measure of the suitability of a calibration curve. It is not necessary to evaluate both the RSE and the correlation coefficient.

(xi) Changes in equipment such as equipment from a vendor different from the one specified in the method.

(xii) The use of micro or midi distillation apparatus in place of macro distillation apparatus.

(xiii) The use of prepackaged reagents.

(xiv) The use of digital titrators and methods where the underlying chemistry used for the determination is similar to that used in the approved method.

(xv) Use of selected ion monitoring (SIM) mode for analytes that cannot be effectively analyzed in full-scan mode and reach the required sensitivity. False positives are more of a concern when using SIM analysis, so at a minimum, one quantitation and two qualifying ions must be monitored for each analyte (unless fewer than three ions with intensity greater than 15% of the base peak are available). The ratio of each of the two qualifying ions to the quantitation ion must be evaluated and should agree with the ratio observed in an authentic standard within ±20 percent. Analyst judgment must be applied to the evaluation of ion ratios because the ratios can be affected by co-eluting compounds present in the sample matrix. The signal-to-noise ratio of the least sensitive ion should be at least 3:1. Retention time in the sample should match within 0.05 minute of an authentic standard analyzed under identical conditions. Matrix interferences can cause minor shifts in retention time and may be evident as shifts in the retention times of the internal standards. The total scan time should be such that a minimum of eight scans are obtained per chromatographic peak.

(xvi) Changes are allowed in purge-and-trap sample volumes or operating conditions. Some examples are:

(A) Changes in purge time and purge-gas flow rate. A change in purge time and purge-gas flow rate is allowed provided that sufficient total purge volume is used to achieve the required minimum detectible concentration and calibration range for all compounds. In general, a purge rate in the range 20–200 mL/min and a total purge volume in the range 240–880 mL are recommended.

(B) Use of nitrogen or helium as a purge gas, provided that the required sensitivities for all compounds are met.

(C) Sample temperature during the purge state. Gentle heating of the sample during purging (*e.g.,* 40 °C) increases purging efficiency of hydrophilic compounds and may improve sample-to-sample repeatability because all samples are purged under precisely the same conditions.

(D) Trap sorbent. Any trap design is acceptable, provided that the data acquired meet all QC criteria.

(E) Changes to the desorb time. Shortening the desorb time (*e.g.,* from 4 minutes to 1 minute) may not affect compound recoveries, and can shorten overall cycle time and significantly reduce the amount of water introduced to the analytical system, thus improving the precision of analysis, especially for water-soluble analytes. A desorb time of four minutes is recommended, however a shorter desorb time may be used, provided that all QC specifications in the method are met.

(F) Use of water management techniques is allowed. Water is always collected on the trap along with the analytes and is a significant interference for analytical systems (GC and GC/MS). Modern water management techniques (*e.g.,* dry purge or condensation points) can remove moisture from the sample stream and improve analytical performance.

(xvii) The following modifications are allowable when performing EPA Method 625: The base/neutral and acid fractions may be added together and analyzed as one extract, provided that the analytes can be reliably identified and quantified in the combined extracts; the pH extraction sequence may be reversed to better separate acid and neutral components; neutral components may be extracted with either acid or base components; a smaller sample volume may be used to minimize matrix interferences provided matrix interferences are demonstrated and documented; alternative surrogate and internal standard concentrations other than those specified in the method are acceptable, provided that method performance is not degraded; an alternative concentration range may be used for the calibration other than the range specified in the method; the solvent for the calibration standards may be changed to match the solvent of the final sample extract.

(xviii) If the characteristics of a wastewater matrix prevent efficient recovery of organic pollutants and prevent the method from meeting QC requirements, the analyst may attempt to resolve the issue by adding salts to the sample, provided that such salts do not react with or introduce the target pollutant into the sample (as evidenced by the analysis of method blanks, laboratory control samples, and spiked samples that also contain such salts), and that all requirements of paragraph (b)(2) of this section are met. Samples having residual chlorine or other halogen must be dechlorinated prior to the addition of such salts.

(xix) If the characteristics of a wastewater matrix result in poor sample dispersion or reagent deposition on equipment and prevent the analyst from meeting QC requirements, the analyst may attempt to resolve the issue by adding a inert surfactant that does not affect the chemistry of the method, such as Brij-35 or sodium dodecyl sulfate (SDS), provided that such surfactant does not react with or introduce the target pollutant into the sample (as evidenced by the analysis of method blanks, laboratory control samples, and spiked samples that also contain such surfactant) and that all requirements of paragraph (b)(1) and (b)(2) of this section are met. Samples having residual chlorine or other halogen must be dechlorinated prior to the addition of such surfactant.

(xx) The use of gas diffusion (using pH change to convert the analyte to gaseous form and/or heat to separate an analyte contained in steam from the sample matrix) across a hydrophobic semi-permeable membrane to separate the analyte of interest from the sample matrix may be used in place of manual or automated distillation in methods for analysis such as ammonia, total cyanide, total Kjeldahl nitrogen, and total phenols. These procedures do not replace the digestion procedures specified in the approved methods and must be used in conjunction with those procedures.

(xxi) Changes in equipment operating parameters such as the monitoring wavelength of a colorimeter or the reaction time and temperature as needed to achieve the chemical reactions defined in the unmodified CWA method. For example, molybdenum blue phosphate methods have two absorbance maxima, one at about 660 nm and another at about 880 nm. The former is about 2.5 times less sensitive than the latter. Wavelength choice provides a cost-effective, dilution-free means to increase sensitivity of molybdenum blue phosphate methods.

(xxii) Interchange of oxidants, such as the use of titanium oxide in UV-assisted automated digestion of TOC and total phosphorus, as long as complete oxidation can be demonstrated.

(xxii) Use of an axially viewed torch with Method 200.7.

■ 7. Add new § 136.7 to read as follows:

§ 136.7 Quality assurance and quality control.

The permittee/laboratory shall use suitable QA/QC procedures when conducting compliance analyses with any Part 136 chemical method or an alternative method specified by the permitting authority. These QA/QC procedures are generally included in the analytical method or may be part of the methods compendium for approved Part 136 methods from a consensus organization. For example, Standard Methods contains QA/QC procedures in the Part 1000 section of the Standard Methods Compendium. The permittee/laboratory shall follow these QA/QC procedures, as described in the method or methods compendium. If the method lacks QA/QC procedures, the permittee/laboratory has the following options to comply with the QA/QC requirements:

(a) Refer to and follow the QA/QC published in the ''equivalent'' EPA method for that parameter that has such QA/QC procedures;

(b) Refer to the appropriate QA/QC section(s) of an approved Part 136 method from a consensus organization compendium;

(c)(1) Incorporate the following twelve quality control elements, where applicable, into the laboratory's documented standard operating procedure (SOP) for performing compliance analyses when using an approved Part 136 method when the method lacks such QA/QC procedures. One or more of the twelve QC elements may not apply to a given method and may be omitted if a written rationale is provided indicating why the element(s) is/are inappropriate for a specific method.

(i) Demonstration of Capability (DOC);

(ii) Method Detection Limit (MDL);

(iii) Laboratory reagent blank (LRB), also referred to as method blank (MB);

(iv) Laboratory fortified blank (LFB), also referred to as a spiked blank, or laboratory control sample (LCS);

(v) Matrix spike (MS) and matrix spike duplicate (MSD), or laboratory fortified matrix (LFM) and LFM duplicate, may be used for suspected matrix interference problems to assess precision;

(vi) Internal standards (for GC/MS analyses), surrogate standards (for organic analysis) or tracers (for radiochemistry);

(vii) Calibration (initial and continuing), also referred to as initial calibration verification (ICV) and continuing calibration verification (CCV);

(viii) Control charts (or other trend analyses of quality control results);

(ix) Corrective action (root cause analysis);

(x) QC acceptance criteria;

(xi) Definitions of preparation and analytical batches that may drive QC frequencies; and

(xii) Minimum frequency for conducting all QC elements.

(2) These twelve quality control elements must be clearly documented in the written standard operating procedure for each analytical method not containing QA/QC procedures, where applicable.

■ 8. Revise Appendix C to Part 136 to read as follows:

APPENDIX C TO PART 136—DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA–ATOMIC EMISSION SPECTROMETRY METHOD 200.7

1.0 Scope and Application

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP–AES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, wastewater, and solid wastes.[1–4] (For analysis of petroleum products see References 5 and 6, Section 16.0). This method is applicable to the following analytes:

Analyte	Chemical abstract services registry number (CASRN)
Aluminum (Al)	7429–90–5
Antimony (Sb)	7440–36–0
Arsenic (As)	7440–38–2
Barium (Ba)	7440–39–3
Beryllium (Be)	7440–41–7
Boron (B)	7440–42–8
Cadmium (Cd)	7440–43–9
Calcium (Ca)	7440–70–2
Cerium[a] (Cr)	7440–45–1
Chromium (Cr)	7440–47–3
Cobalt (Co)	7440–48–4
Copper (Cu)	7440–50–8
Iron (Fe)	7439–89–6
Lead (Pb)	7439–92–1
Lithium (Li)	7439–93–2
Magnesium (Mg)	7439–95–4
Manganese (Mn)	7439–96–5
Mercury (Hg)	7439–97–6
Molybdenum (Mo)	7439–98–7
Nickel (Ni)	7440–02–0
Phosphorus (P)	7723–14–0
Potassium (K)	7440–09–7
Selenium (Se)	7782–49–2
Silica[b] (SiO_2)	7631–86–9
Silver (Ag)	7440–22–4
Sodium (Na)	7440–23–5
Strontium (Sr)	7440–24–6
Thallium (Tl)	7440–28–0
Tin (Sn)	7440–31–5
Titanium (Ti)	7440–32–6
Vanadium (V)	7440–62–2
Zinc (Zn)	7440–66–6

[a] Cerium has been included as method analyte for correction of potential interelement spectral interference.

[b] This method is *not* suitable for the determination of silica in solids.

1.2 For reference where this method is approved for use in compliance monitoring programs [*e.g.,* Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest **Federal Register** announcements.

1.3 ICP–AES can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, dissolved solids should be <0.2% (w/v) (Section 4.2).

1.4 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of <1 NTU at the time of analysis. This total recoverable determination procedure is referred to as ''direct analysis''. However, in the determination of some primary drinking water metal contaminants, preconcentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria (Sections 11.2.2 through 11.2.7).

1.5 For the determination of total recoverable analytes in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (*e.g.,* soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material 1% (w/v) should be extracted as a solid type sample.

1.6 When determining boron and silica in aqueous samples, only plastic, PTFE or quartz labware should be used from time of sample collection to completion of analysis. For accurate determination of boron in solid samples only quartz or PTFE beakers should be used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.

1.7 Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by ''direct analysis'' where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver.

The total recoverable sample digestion procedure given in this method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains <0.1 mg/L silver. The extraction of solid samples containing concentrations of silver >50 mg/kg should be treated in a similar manner. Also, the extraction of tin from solid samples should be prepared again using aliquots <1 g when determined sample concentrations exceed 1%.

1.8 The total recoverable sample digestion procedure given in this method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

1.9 The total recoverable sample digestion procedure given in this method is not suitable for the determination of volatile organo-mercury compounds. However, if digestion is not required (turbidity <1 NTU), the combined concentrations of inorganic and organo-mercury in solution can be determined by ''direct analysis'' pneumatic nebulization provided the sample solution is adjusted to contain the same mixed acid (HNO_3 + HCl) matrix as the total recoverable calibration standards and blank solutions.

1.10 Detection limits and linear ranges for the elements will vary with the wavelength selected, the spectrometer, and the matrices. Table 1 provides estimated instrument detection limits for the listed wavelengths.[7] However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation, and selected operating conditions.

1.11 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must document and have on file the required initial demonstration performance data described in Section 9.2 prior to using the method for analysis.

2.0 Summary of Method

2.1 An aliquot of a well mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the ''direct analysis'' total recoverable determination of analytes in drinking water where sample turbidity is <1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

2.2 The analysis described in this method involves multielemental determinations by ICP–AES using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. Background must be measured adjacent to the analyte wavelength during analysis. Various interferences must be considered and addressed appropriately as discussed in Sections 4.0, 7.0, 9.0, 10.0, and 11.0.

3.0 Definitions

3.1 Calibration Blank—A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument (Section 7.10.1).

3.2 Calibration Standard (CAL)—A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration (Section 7.9).

3.3 Dissolved Analyte—The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification (Section 11.1).

3.4 Field Reagent Blank (FRB)—An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment (Section 8.5).

3.5 Instrument Detection Limit (IDL)—The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the same wavelength (Table 1.).

3.6 Instrument Performance Check (IPC) Solution—A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria (Sections 7.11 and 9.3.4).

3.7 Internal Standard—Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component (Section 11.5).

3.8 Laboratory Duplicates (LD1 and LD2)—Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.9 Laboratory Fortified Blank (LFB)—An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements (Sections 7.10.3 and 9.3.2).

3.10 Laboratory Fortified Sample Matrix (LFM)—An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations (Section 9.4).

3.11 Laboratory Reagent Blank (LRB)—An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus (Sections 7.10.2 and 9.3.1).

3.12 Linear Dynamic Range (LDR)—The concentration range over which the instrument response to an analyte is linear (Section 9.2.2).

3.13 Method Detection Limit (MDL)—The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero (Section 9.2.4 and Table 4.).

3.14 Plasma Solution—A solution that is used to determine the optimum height above the work coil for viewing the plasma (Sections 7.15 and 10.2.3).

3.15 Quality Control Sample (QCS)—A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance (Sections 7.12 and 9.2.3).

3.16 Solid Sample—For the purpose of this method, a sample taken from material classified as soil, sediment or sludge.

3.17 Spectral Interference Check (SIC) Solution—A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria (Sections 7.13, 7.14 and 9.3.5).

3.18 Standard Addition—The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration (Sections 9.5.1 and 11.5).

3.19 Stock Standard Solution—A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source (Section 7.8).

3.20 Total Recoverable Analyte—The concentration of analyte determined either by ''direct analysis'' of an unfiltered acid preserved drinking water sample with turbidity of <1 NTU (Section 11.2.1), or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Sections 11.2 and 11.3).

3.21 Water Sample—For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

4.0 Interferences

4.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate not only when alternate wavelengths are desirable because of severe spectral interference, but also will show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by the measured emission on one side or the other. The location(s) selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The location(s) used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.

4.1.2 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for interelement contributions, which involves measuring the interfering elements. Some potential on-line spectral interferences observed for the recommended wavelengths are given in Table 2. When operative and uncorrected, these interferences will produce false-positive determinations and be reported as analyte concentrations. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature that were observed with a single instrument having a working resolution of 0.035 nm are listed. More extensive information on interferant effects at various wavelengths and resolutions is available in Boumans' Tables.[8] Users may apply interelement correction factors determined on their instruments within tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements.

4.1.3 When interelement corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions as described in Section 7.13. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.[7,8]

4.1.4 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths given in Table 1, the analyst is required to determine and document for each wavelength the effect from the known interferences given in Table 2, and to utilize a computer routine for their automatic correction on all analyses. To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for their automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference effect from all method analytes and provide for their automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient, however, for analytes such as iron that may be found at high concentration a more appropriate test would be to use a concentration near the upper LDR limit. See Section 10.4 for required spectral interference test criteria.

4.1.5 When interelement corrections are not used, either on-going SIC solutions (Section 7.14) must be analyzed to verify the absence of interelement spectral interference or a computer software routine must be employed for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, greater than the analyte IDL, or false negative analyte concentration, less than the 99% lower control limit of the calibration blank. When the interference accounts for 10% or more of the analyte concentration, either an alternate wavelength free of interference or another approved test procedure must be used to complete the analysis. For example, the copper peak at 213.853 nm could be mistaken for the zinc peak at 213.856 nm in solutions with high copper and low zinc concentrations. For this example, a spectral scan in the 213.8 nm region would not reveal the misidentification because a single peak near the zinc location would be observed. The possibility of this misidentification of copper for the zinc peak at 213.856 nm can be identified by measuring the copper at another emission line, *e.g.,* 324.754 nm. Users should be aware that, depending upon the instrumental resolution, alternate wavelengths with adequate sensitivity and freedom from interference may not be available for all matrices. In these circumstances the analyte must be determined using another approved test procedure.

4.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by such means as a high-solids nebulizer, diluting the sample, using a peristaltic pump, or using an appropriate internal standard element. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. This problem can be controlled by a high-solids nebulizer, wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rates, especially for the nebulizer, improves instrument stability and precision; this is accomplished with the use of mass flow controllers.

4.3 Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP–AES technique. If observed, they can be minimized by careful selection of operating conditions (such as incident power and observation height), by buffering of the sample, by matrix matching, and by standard-addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (Section 7.10.4). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to either their LDR or a concentration ten times those usually encountered. The aspiration time should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit, should be noted. Until the required rinse time is established, this method requires a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be re-analyzed after a long rinse period.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.[9–12] A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Specifically, concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

5.2 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

5.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.

5.4 The inductively coupled plasma should only be viewed with proper eye protection from the ultraviolet emissions.

5.5 It is the responsibility of the user of this method to comply with relevant disposal and waste regulations. For guidance see Sections 14.0 and 15.0.

6.0 Equipment and Supplies

6.1 Inductively coupled plasma emission spectrometer:

6.1.1 Computer-controlled emission spectrometer with background-correction capability.

The spectrometer must be capable of meeting and complying with the requirements described and referenced in Section 2.2.

6.1.2 Radio-frequency generator compliant with FCC regulations.

6.1.3 Argon gas supply—High purity grade (99.99%). When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional cylinders.

6.1.4 A variable speed peristaltic pump is required to deliver both standard and sample solutions to the nebulizer.

6.1.5 (Optional) Mass flow controllers to regulate the argon flow rates, especially the aerosol transport gas, are highly recommended. Their use will provide more exacting control of reproducible plasma conditions.

6.2 Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.

6.3 A temperature adjustable hot plate capable of maintaining a temperature of 95 °C.

6.4 (Optional) A temperature adjustable block digester capable of maintaining a temperature of 95 °C and equipped with 250 mL constricted digestion tubes.

6.5 (Optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

6.6 A gravity convection drying oven with thermostatic control capable of maintaining 180 °C ± 5 °C.

6.7 (Optional) An air displacement pipetter capable of delivering volumes ranging from 0.1–2500 µL with an assortment of high quality disposable pipet tips.

6.8 Mortar and pestle, ceramic or nonmetallic material.

6.9 Polypropylene sieve, 5-mesh (4 mm opening).

6.10 Labware—For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by contributing contaminants through surface desorption or leaching, or depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Several procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for four hours or more in 20% (v/v) nitric acid or a mixture of HNO_3 and HCl (1+2+9), rinsing with reagent water and storing clean.[2 3] Chromic acid cleaning solutions must be avoided because chromium is an analyte.

6.10.1 Glassware—Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).

6.10.2 Assorted calibrated pipettes.

6.10.3 Conical Phillips beakers (Corning 1080–250 or equivalent), 250 mL with 50 mm watch glasses.

6.10.4 Griffin beakers, 250 mL with 75 mm watch glasses and (optional) 75 mm ribbed watch glasses.

6.10.5 (Optional) PTFE and/or quartz Griffin beakers, 250 mL with PTFE covers.

6.10.6 Evaporating dishes or high-form crucibles, porcelain, 100 mL capacity.

6.10.7 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125 mL to 1 L capacities.

6.10.8 One-piece stem FEP wash bottle with screw closure, 125 mL capacity.

7.0 Reagents and Standards

7.1 Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society specifications[13] should be used whenever possible. If the purity of a reagent is in question, analyze for contamination. All acids used for this method must be of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers. Redistilled acids prepared by sub-boiling distillation are acceptable.

7.2 Hydrochloric acid, concentrated (sp.gr. 1.19)—HCl.

7.2.1 Hydrochloric acid (1+1)—Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.2 Hydrochloric acid (1+4)—Add 200 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.3 Hydrochloric acid (1+20)—Add 10 mL concentrated HCl to 200 mL reagent water.

7.3 Nitric acid, concentrated (sp.gr. 1.41)—HNO_3.

7.3.1 Nitric acid (1+1)—Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1 L.

7.3.2 Nitric acid (1+2)—Add 100 mL concentrated HNO_3 to 200 mL reagent water.

7.3.3 Nitric acid (1+5)—Add 50 mL concentrated HNO_3 to 250 mL reagent water.

7.3.4 Nitric acid (1+9)—Add 10 mL concentrated HNO_3 to 90 mL reagent water.

7.4 Reagent water. All references to water in this method refer to ASTM Type I grade water.[14]

7.5 Ammonium hydroxide, concentrated (sp.gr. 0.902).

7.6 Tartaric acid, ACS reagent grade.

7.7 Hydrogen peroxide, 50%, stabilized certified reagent grade.

7.8 Standard Stock Solutions—Stock standards may be purchased or prepared from ultra-high purity grade chemicals (99.99–99.999% pure). All compounds must be dried for one hour at 105 °C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards cannot be verified.

CAUTION: Many of these chemicals are extremely toxic if inhaled or swallowed (Section 5.1). Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow for 1 L quantities, but for the purpose of pollution prevention, the analyst is encouraged to prepare smaller quantities when possible. Concentrations are calculated based upon the weight of the pure element or upon the weight of the compound multiplied by the fraction of the analyte in the compound

From pure element,

$$\text{Concentration} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

From pure compound,

$$\text{Concentration} = \frac{\text{weight (mg)} \times \text{gravimetric factor}}{\text{volume (L)}}$$

where: gravimetric factor = the weight fraction of the analyte in the compound

7.8.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1+1) HCl and 1 mL of concentrated HNO_3 in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1 L flask, add an additional 10.0 mL of (1+1) HCl and dilute to volume with reagent water.

7.8.2 Antimony solution, stock, 1 mL = 1000 µg Sb: Dissolve 1.000 g of antimony powder, weighed accurately to at least four significant figures, in 20.0 mL (1+1) HNO_3 and 10.0 mL concentrated HCl. Add 100 mL reagent water and 1.50 g tartaric acid. Warm solution slightly to effect complete dissolution. Cool solution and add reagent water to volume in a 1 L volumetric flask.

7.8.3 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 1.320 g of As_2O_3 (As fraction = 0.7574), weighed accurately to at least four significant figures, in 100 mL of reagent water containing 10.0 mL concentrated NH_4OH. Warm the solution gently to effect dissolution. Acidify the solution with 20.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 1.437 g $BaCO_3$ (Ba fraction = 0.6960), weighed accurately to at least four significant figures, in 150 mL (1+2) HNO_3 with heating and stirring to degas and dissolve compound. Let solution cool and dilute with reagent water in 1 L volumetric flask.

7.8.5 Beryllium solution, stock, 1 mL = 1000 µg Be: *DO NOT DRY.* Dissolve 19.66 g $BeSO_4 \bullet 4H_2O$ (Be fraction = 0.0509), weighed accurately to at least four significant figures, in reagent water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.6 Boron solution, stock, 1 mL = 1000 µg B: *DO NOT DRY.* Dissolve 5.716 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1 L volumetric flask with reagent water. Transfer immediately after mixing to a clean FEP bottle to minimize any leaching of boron from the glass volumetric container. Use of a nonglass volumetric flask is recommended to avoid boron contamination from glassware.

7.8.7 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 1.000 g Cd metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.8.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.498 g $CaCO_3$ (Ca fraction = 0.4005), dried at 180 °C for one hour before weighing, weighed accurately to at least four significant figures, in reagent water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.9 Cerium solution, stock, 1 mL = 1000 µg Ce: Slurry 1.228 g CeO_2 (Ce fraction = 0.8141), weighed accurately to at least four significant figures, in 100 mL concentrated HNO_3 and evaporate to dryness. Slurry the residue in 20 mL H_2O, add 50 mL concentrated HNO_3, with heat and stirring add 60 mL 50% H_2O_2 dropwise in 1 mL increments allowing periods of stirring between the 1 mL additions. Boil off excess H_2O_2 before diluting to volume in a 1 L volumetric flask with reagent water.

7.8.10 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.923 g CrO_3 (Cr fraction = 0.5200), weighed accurately to at least four significant figures, in 120 mL (1+5) HNO_3. When solution is complete, dilute to volume in a 1 L volumetric flask with reagent water.

7.8.11 Cobalt solution, stock, 1 mL = 1000 µg Co: Dissolve 1.000 g Co metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50.0 mL (1+1) HNO_3. Let solution cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.12 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.000 g Cu metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50.0 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute in a 1 L volumetric flask with reagent water.

7.8.13 Iron solution, stock, 1 mL = 1000 µg Fe: Dissolve 1.000 g Fe metal, acid cleaned with (1+1) HCl, weighed accurately to four significant figures, in 100 mL (1+1) HCl with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.8.14 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 1.599 g $Pb(NO_3)_2$ (Pb fraction = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1+1) HNO_3. Add 20.0 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.15 Lithium solution, stock, 1 mL = 1000 µg Li: Dissolve 5.324 g Li_2CO_3 (Li fraction = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1+1) HCl and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.16 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 1.000 g cleanly polished Mg ribbon, accurately weighed to at least four significant figures, in slowly added 5.0 mL (1+1) HCl (CAUTION: reaction is vigorous). Add 20.0 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.17 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 1.000 g of manganese metal, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.18 Mercury solution, stock, 1 mL = 1000 µg Hg: *DO NOT DRY.* CAUTION: highly toxic element. Dissolve 1.354 g $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated HNO_3 and dilute to volume in 1 L volumetric flask with reagent water.

7.8.19 Molybdenum solution, stock, 1 mL = 1000 µg Mo: Dissolve 1.500 g MoO_3 (Mo fraction = 0.6666), weighed accurately to at least four significant figures, in a mixture of 100 mL reagent water and 10.0 mL concentrated NH_4OH, heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.8.20 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 1.000 g of nickel metal, weighed accurately to at least four significant figures, in 20.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.21 Phosphorus solution, stock, 1 mL = 1000 µg P: Dissolve 3.745 g $NH_4H_2PO_4$ (P fraction = 0.2696), weighed accurately to at least four significant figures, in 200 mL reagent water and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.22 Potassium solution, stock, 1 mL = 1000 µg K: Dissolve 1.907 g KCl (K fraction = 0.5244) dried at 110 °C, weighed accurately to at least four significant figures, in reagent water, add 20 mL (1+1) HCl and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.23 Selenium solution, stock, 1 mL = 1000 µg Se: Dissolve 1.405 g SeO_2 (Se fraction = 0.7116), weighed accurately to at least four significant figures, in 200 mL reagent water and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.24 Silica solution, stock, 1 mL = 1000 µg SiO_2: *DO NOT DRY.* Dissolve 2.964 g $(NH_4)_2SiF_6$, weighed accurately to at least four significant figures, in 200 mL (1+20) HCl with heating at 85 °C to effect dissolution. Let solution cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.25 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 1.000 g Ag metal, weighed accurately to at least four significant figures, in 80 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask. Store solution in amber bottle or wrap bottle completely with aluminum foil to protect solution from light.

7.8.26 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 2.542 g NaCl (Na fraction = 0.3934), weighed accurately to at least four significant figures, in reagent water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.27 Strontium solution, stock, 1 mL = 1000 µg Sr: Dissolve 1.685 g $SrCO_3$ (Sr fraction = 0.5935), weighed accurately to at least four significant figures, in 200 mL reagent water with dropwise addition of 100 mL (1+1) HCl. Dilute to volume in a 1 L volumetric flask with reagent water.

7.8.28 Thallium solution, stock, 1 mL = 1000 µg Tl: Dissolve 1.303 g $TlNO_3$ (Tl fraction = 0.7672), weighed accurately to at least four significant figures, in reagent water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.29 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least four significant figures, in an acid mixture of 10.0 mL concentrated HCl and 2.0 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool, add 200 mL concentrated HCl, and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.30 Titanium solution, stock, 1 mL = 1000 µg Ti: *DO NOT DRY.* Dissolve 6.138 g $(NH_4)_2TiO(C_2O_4)_2 \bullet H_2O$ (Ti fraction = 0.1629), weighed accurately to at least four significant figures, in 100 mL reagent water. Dilute to volume in a 1 L volumetric flask with reagent water.

7.8.31 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 1.000 g V metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water to volume in a 1 L volumetric flask.

7.8.32 Yttrium solution, stock 1 mL = 1000 µg Y: Dissolve 1.270 g Y_2O_3 (Y fraction = 0.7875), weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3, heating to effect dissolution. Cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.33 Zinc solution, stock, 1 mL = 1000 µg Zn: Dissolve 1.000 g Zn metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water to volume in a 1 L volumetric flask.

7.9 Mixed Calibration Standard Solutions—For the analysis of total recoverable digested samples prepare mixed calibration standard solutions (see Table 3) by combining appropriate volumes of the stock solutions in 500 mL volumetric flasks containing 20 mL (1+1) HNO_3 and 20 mL (1+1) HCl and dilute to volume with reagent water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. To minimize the opportunity for contamination by the containers, it is recommended to transfer the mixed-standard solutions to acid-cleaned, never-used FEP fluorocarbon (FEP) bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentrations can change on aging. Calibration standards not prepared from primary standards must be initially verified using a certified reference solution. For the recommended wavelengths listed in Table 1 some typical calibration standard combinations are given in Table 3.

NOTE: If the addition of silver to the recommended mixed-acid calibration standard results in an initial precipitation, add 15 mL of reagent water and warm the flask until the solution clears. For this acid combination, the silver concentration should be limited to 0.5 mg/L.

7.10 Blanks—Four types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure, the laboratory fortified blank is used to assess routine laboratory performance and a rinse blank is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

7.10.1 The calibration blank for aqueous samples and extracts is prepared by acidifying reagent water to the same concentrations of the acids as used for the standards. The calibration blank should be stored in a FEP bottle.

7.10.2 The laboratory reagent blank (LRB) must contain all the reagents in the same volumes as used in the processing of the samples. The LRB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

7.10.3 The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all analytes to a suitable concentration using the following recommended criteria: Ag 0.1 mg/L, K 5.0 mg/L and all other analytes 0.2 mg/L or a concentration approximately 100 times their respective MDL, whichever is greater. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

7.10.4 The rinse blank is prepared by acidifying reagent water to the same concentrations of acids as used in the calibration blank and stored in a convenient manner.

7.11 Instrument Performance Check (IPC) Solution—The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method analytes at appropriate concentrations. Silver must be limited to <0.5 mg/L; while potassium and phosphorus because of higher MDLs and silica because of potential contamination should be at concentrations of 10 mg/L. For other analytes a concentration of 2 mg/L is recommended. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in an FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

7.12 Quality Control Sample (QCS)—Analysis of a QCS is required for initial and periodic verification of calibration standards or stock standard solutions in order to verify instrument performance. The QCS must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the analytes in the QCS solution should be 1 mg/L, except silver, which must be limited to a concentration of 0.5 mg/L for solution stability. The QCS solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed.

7.13 Spectral Interference Check (SIC) Solutions—When interelement corrections are applied, SIC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors.

7.13.1 SIC solutions containing (a) 300 mg/L Fe; (b) 200 mg/L AL; (c) 50 mg/L Ba; (d) 50 mg/L Be; (e) 50 mg/L Cd; (f) 50 mg/L Ce; (g) 50 mg/L Co; (h) 50 mg/L Cr; (i) 50 mg/L Cu; (j) 50 mg/L Mn; (k) 50 mg/L Mo; (l) 50 mg/L Ni; (m) 50 mg/L Sn; (n) 50 mg/L SiO_2; (o) 50 mg/L Ti; (p) 50 mg/L Tl and (q) 50 mg/L V should be prepared in the same acid mixture as the calibration standards and stored in FEP bottles. These solutions can be used to periodically verify a partial list of the on-line (and possible off-line) interelement spectral correction factors for the recommended wavelengths given in Table 1. Other solutions could achieve the same objective as well. (Multielement SIC solutions[3] may be prepared and substituted for the single element solutions provided an analyte is not subject to interference from more than one interferant in the solution.)

Note: If wavelengths other than those recommended in Table 1 are used, other solutions different from those above (a through q) may be required.

7.13.2 For interferences from iron and aluminum, only those correction factors (positive or negative) when multiplied by 100 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

7.13.3 For the other interfering elements, only those correction factors (positive or negative) when multiplied by 10 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

7.13.4 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution (a through q) should fall within a specific concentration range bracketing the calibration blank. This concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after subtraction of the calibration blank the apparent analyte concentration is outside (above or below) this range, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor should be updated.

Note: The SIC solution should be analyzed more than once to confirm a change has occurred with adequate rinse time between solutions and before subsequent analysis of the calibration blank.

7.13.5 If the correction factors tested on a daily basis are found to be within the 10% criteria for five consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such (*e.g.,* finished drinking water) that they do not contain concentrations of the interfering elements at the 10 mg/L level, daily verification is not required; however, all interelement spectral correction factors must be verified annually and updated, if necessary.

7.13.6 If the instrument does not display negative concentration values, fortify the SIC solutions with the elements of interest at 1 mg/L and test for analyte recoveries that are below 95%. In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero.

7.14 For instruments without interelement correction capability or when interelement corrections are not used, SIC solutions (containing similar concentrations of the major components in the samples, *e.g.,* 10 mg/L) can serve to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the SIC solution confirms an operative interference that is 10% of the analyte concentration, the analyte must be determined using a wavelength and background correction location free of the interference or by another approved test procedure. Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests.

7.15 Plasma Solution—The plasma solution is used for determining the optimum viewing height of the plasma above the work coil prior to using the method (Section 10.2). The solution is prepared by adding a 5 mL aliquot from each of the stock standard solutions of arsenic, lead, selenium, and thallium to a mixture of 20 mL (1+1) nitric acid and 20 mL (1+1) hydrochloric acid and diluting to 500 mL with reagent water. Store in a FEP bottle.

8.0 Sample Collection, Preservation, and Storage

8.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (*i.e.,* dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to aliquoting for processing or ''direct analysis'' to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to six months before analysis.

8.2 For the determination of the dissolved elements, the sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH <2.

8.3 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1+1) nitric acid to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH <2 just prior withdrawing an aliquot for processing or ''direct analysis''. If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added and the sample held for 16 hours until verified to be pH <2. See Section 8.1.

Note: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood. See Section 5.2.

8.4 Solid samples require no preservation prior to analysis other than storage at 4 °C. There is no established holding time limitation for solid samples.

8.5 For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

9.0 Quality Control

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

9.2 Initial Demonstration of Performance (mandatory).

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to analyses conducted by this method.

9.2.2 Linear dynamic range (LDR)—The upper limit of the LDR must be established for each wavelength utilized. It must be determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. The LDR should be determined by analyzing succeedingly higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% below the stated concentration of the standard. Determined LDRs must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed. The LDRs should be verified annually or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.2.3 Quality control sample (QCS)—When beginning the use of this method, on a quarterly basis, after the preparation of stock or calibration standard solutions or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS (Section 7.12). To verify the calibration standards the determined mean concentrations from three analyses of the QCS must be within 5% of the stated values. If the calibration standard cannot be verified, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding on with the initial determination of method detection limits or continuing with on-going analyses.

9.2.4 Method detection limit (MDL)—MDLs must be established for all wavelengths utilized, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit.[15] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

Where:

t = students' t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]

S = standard deviation of the replicate analyses

Note: If additional confirmation is desired, reanalyze the seven replicate aliquots on two more nonconsecutive days and again calculate the MDL values for each day. An average of the three MDL values for each analyte may provide for a more appropriate MDL estimate. If the relative standard deviation (RSD) from the analyses of the seven aliquots is <10%, the concentration used to determine the analyte MDL may have been inappropriately high for the determination. If so, this could result in the calculation of an unrealistically low MDL. Concurrently, determination of MDL in reagent water represents a best case situation and does not reflect possible matrix effects of real world samples. However, successful analyses of LFMs (Section 9.4) and the analyte addition test described in Section 9.5.1 can give confidence to the MDL value determined in reagent water. Typical single laboratory MDL values using this method are given in Table 4.

The MDLs must be sufficient to detect analytes at the required levels according to compliance monitoring regulation (Section 1.2). MDLs should be determined annually, when a new operator begins work or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.3 Assessing Laboratory Performance (mandatory)

9.3.1 Laboratory reagent blank (LRB)—The laboratory must analyze at least one LRB (Section 7.10.2) with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the MDL indicate laboratory or reagent contamination should be suspected. When LRB values constitute 10% or more of the analyte level determined for a sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.

9.3.2 Laboratory fortified blank (LFB)—The laboratory must analyze at least one LFB (Section 7.10.3) with each batch of samples. Calculate accuracy as percent recovery using the following equation:

$$R = \frac{LFB - LRB}{s} \times 100$$

Where:

R = percent recovery
LFB = laboratory fortified blank
LRB = laboratory reagent blank
s = concentration equivalent of analyte added to fortify the LBR solution

If the recovery of any analyte falls outside the required control limits of 85–115%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 85–115% (Section 9.3.2). When sufficient internal performance data become available (usually a minimum of 20–30 analyses), optional control limits can be developed from the mean percent recovery (x) and the standard deviation (S) of the mean percent recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x − 3S

The optional control limits must be equal to or better than the required control limits of 85–115%. After each five to 10 new recovery measurements, new control limits can be calculated using only the most recent 20–30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4 Instrument performance check (IPC) solution—For all determinations the laboratory must analyze the IPC solution (Section 7.11) and a calibration blank immediately following daily calibration, after every 10th sample (or more frequently, if required) and at the end of the sample run. Analysis of the calibration blank should always be < the analyte IDL, but greater than the lower 3-sigma control limit of the calibration blank. Analysis of the IPC solution immediately following calibration must verify that the instrument is within 5% of calibration with a relative standard deviation <3% from replicate integrations 4. Subsequent analyses of the IPC solution must be within 10% of calibration. If the calibration cannot be verified within the specified limits, reanalyze either or both the IPC solution and the calibration blank. If the second analysis of the IPC solution or the calibration blank confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected and/or the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.3.5 Spectral interference check (SIC) solution—For all determinations the laboratory must periodically verify the interelement spectral interference correction routine by analyzing SIC solutions. The preparation and required periodic analysis of SIC solutions and test criteria for verifying the interelement interference correction routine are given in Section 7.13. Special cases where on-going verification is required are described in Section 7.14.

9.4 Assessing Analyte Recovery and Data Quality.

9.4.1 Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, laboratory or program, the following laboratory fortified matrix (LFM) procedure (Section 9.4.2) is required. Also, other tests such as the analyte addition test (Section 9.5.1) and sample dilution test (Section 9.5.2) can indicate if matrix effects are operative.

9.4.2 The laboratory must add a known amount of each analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. For water samples, the added analyte concentration must be the same as that used in the laboratory fortified blank (Section 7.10.3). For solid samples, however, the concentration added should be expressed as mg/kg and is calculated for a one gram aliquot by multiplying the added analyte concentration (mg/L) in solution by the conversion factor 100 (mg/L × 0.1L/0.001kg = 100, Section 12.5). (For notes on Ag, Ba, and Sn see Sections 1.7 and 1.8.) Over time, samples from all routine sample sources should be fortified.

Note: The concentration of calcium, magnesium, sodium and strontium in environmental waters, along with iron and aluminum in solids can vary greatly and are not necessarily predictable. Fortifying these analytes in routine samples at the same concentration used for the LFB may prove to be of little use in assessing data quality for these analytes. For these analytes sample dilution and reanalysis using the criteria given in Section 9.5.2 is recommended. Also, if specified by the data user, laboratory or program, samples can be fortified at higher concentrations, but even major constituents should be limited to <25 mg/L so as not to alter the sample matrix and affect the analysis.

9.4.3 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range of 70–130% or a 3-sigma recovery range calculated from the regression equations given in Table 9.[16] Recovery calculations are not required if the concentration added is less than 30% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

Where:

R = percent recovery
C_s = fortified sample concentration
C = sample background concentration
s = concentration equivalent of analyte added to fortify the sample

9.4.4 If the recovery of any analyte falls outside the designated LFM recovery range, and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to either the heterogeneous nature of the sample or matrix effects and analysis by method of standard addition or the use of an internal standard(s) (Section 11.5) should be considered.

9.4.5 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably. Reference materials containing high concentrations of analytes can provide additional information on the performance of the spectral interference correction routine.

9.5 Assess the possible need for the method of standard additions (MSA) or internal standard elements by the following tests. Directions for using MSA or internal standard(s) are given in Section 11.5.

9.5.1 Analyte addition test: An analyte(s) standard added to a portion of a prepared sample, or its dilution, should be recovered to within 85% to 115% of the known value. The analyte(s) addition should produce a minimum level of 20 times and a maximum of 100 times the method detection limit. If the analyte addition is <20% of the sample analyte concentration, the following dilution test should be used. If recovery of the analyte(s) is not within the specified limits, a matrix effect should be suspected, and the associated data flagged accordingly. The method of additions or the use of an appropriate internal standard element may provide more accurate data.

9.5.2 Dilution test: If the analyte concentration is sufficiently high (minimally, a factor of 50 above the instrument detection limit in the original solution but <90% of the linear limit), an analysis of a 1 + 4 dilution should agree (after correction for the fivefold dilution) within 10% of the original determination. If not, a chemical or physical interference effect should be suspected and the associated data flagged accordingly. The method of standard additions or the use of an internal-standard element may provide more accurate data for samples failing this test.

10.0 Calibration and Standardization

10.1 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. However, because of the difference among various makes and models of spectrometers, specific instrument operating conditions cannot be given. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a task. Operating conditions for aqueous solutions usually vary from 1100–1200 watts forward power, 15–16 mm viewing height, 15–19 L/min. argon coolant flow, 0.6–1 L/min. argon aerosol flow, 1–1.8 mL/min. sample pumping rate with a one minute preflush time and measurement time near 1 s per wavelength peak (for sequential instruments) and near 10 s per sample (for simultaneous instruments). Use of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm (by adjusting the argon aerosol flow) has been recommended as a way to achieve repeatable interference correction factors.[17]

10.2 Prior to using this method optimize the plasma operating conditions. The following procedure is recommended for vertically configured plasmas. The purpose of plasma optimization is to provide a maximum signal-to-background ratio for the least sensitive element in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow rate greatly facilitates the procedure.

10.2.1 Ignite the plasma and select an appropriate incident rf power with minimum reflected power. Allow the instrument to become thermally stable before beginning. This usually requires at least 30 to 60 minutes of operation. While aspirating the 1000 µg/mL solution of yttrium (Section 7.8.32), follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5–20 mm above the top of the work coil.[18] Record the nebulizer gas flow rate or pressure setting for future reference.

10.2.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min. by aspirating a known volume calibration blank for a period of at least three minutes. Divide the spent volume by the aspiration time (in minutes) and record the uptake rate. Set the peristaltic pump to deliver the uptake rate in a steady even flow.

10.2.3 After horizontally aligning the plasma and/or optically profiling the spectrometer, use the selected instrument conditions from Sections 10.2.1 and 10.2.2, and aspirate the plasma solution (Section 7.15), containing 10 µg/mL each of As, Pb, Se and Tl. Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14–18 mm above the top of the work coil. (This region of the plasma is commonly referred to as the analytical zone.)[19] Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the largest intensity ratio for the least sensitive element of the four analytes. If more than one position provides the same ratio, select the position that provides the highest net intensity counts for the least sensitive element or accept a compromise position of the intensity ratios of all four analytes.

10.2.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits. Refer to Tables 1 and 4 for comparison of IDLs and MDLs, respectively.

10.2.5 If either the instrument operating conditions, such as incident power and/or nebulizer gas flow rate are changed, or a new torch injector tube having a different orifice i.d. is installed, the plasma and plasma viewing height should be reoptimized.

10.2.6 Before daily calibration and after the instrument warmup period, the nebulizer gas flow must be reset to the determined optimized flow. If a mass flow controller is being used, it should be reset to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same from day-to-day (<2% change). The change in signal intensity with a change in nebulizer gas flow rate for both ''hard'' (Pb 220.353 nm) and ''soft'' (Cu 324.754) lines is illustrated in Figure 1.

10.3 Before using the procedure (Section 11.0) to analyze samples, there must be data available documenting initial demonstration of performance. The required data and procedure is described in Section 9.2. This data must be generated using the same instrument operating conditions and calibration routine (Section 11.4) to be used for sample analysis. These documented data must be kept on file and be available for review by the data user.

10.4 After completing the initial demonstration of performance, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction and for correction of interelement spectral interference in particular are given in Section 4.1. To determine the appropriate location for background correction and to establish the interelement interference correction routine, repeated spectral scan about the analyte wavelength and repeated analyses of the single element solutions may be required. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration on the analyte that is outside the 3-sigma control limits of the calibration blank for the analyte. (The upper-control limit is the analyte IDL.) Once established, the entire routine must be initially and periodically verified annually, or whenever there is a change in instrument operating conditions (Section 10.2.5). Only a portion of the correction routine must be verified more frequently or on a daily basis. Test criteria and required solutions are described in Section 7.13. Initial and periodic verification data of the routine should be kept on file. Special cases where on-going verification are required is described in Section 7.14.

11.0 Procedure

11.1 Aqueous Sample Preparation—Dissolved Analytes

11.1.1 For the determination of dissolved analytes in ground and surface waters, pipet an aliquot (20 mL) of the filtered, acid preserved sample into a 50 mL polypropylene centrifuge tube. Add an appropriate volume of (1 + 1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (*e.g.,* add 0.4 mL (1 + 1) HNO_3 to a 20 mL aliquot of sample). Cap the tube and mix. The sample is now ready for analysis (Section 1.3). Allowance for sample dilution should be made in the calculations. (If mercury is to be determined, a separate aliquot must be additionally acidified to contain 1% (v/v) HCl to match the signal response of mercury in the calibration standard and reduce memory interference effects. Section 1.9).

Note: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be treated using the procedure described in Sections 11.2.2 through 11.2.7 prior to analysis.

11.2 Aqueous Sample Preparation—Total Recoverable Analytes

11.2.1 For the ''direct analysis'' of total recoverable analytes in drinking water samples containing turbidity <1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure described in Section 11.1.1 while making allowance for sample dilution in the data calculation (Section 1.2). For the determination of total recoverable analytes in all other aqueous samples or for preconcentrating drinking water samples prior to analysis follow the procedure given in Sections 11.2.2 through 11.2.7.

11.2.2 For the determination of total recoverable analytes in aqueous samples (other than drinking water with <1 NTU turbidity), transfer a 100 mL (1 mL) aliquot from a well mixed, acid preserved sample to a 250 mL Griffin beaker (Sections 1.2, 1.3, 1.6, 1.7, 1.8, and 1.9). (When necessary, smaller sample aliquot volumes may be used.)

Note: If the sample contains *undissolved* solids >1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid-mixture procedure described in Sections 11.3.3 through 11.3.6.

11.2.3 Add 2 mL (1+1) nitric acid and 1.0 mL of (1+1) hydrochloric acid to the beaker containing the measured volume of sample. Place the beaker on the hot plate for solution evaporation. The hot plate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85 °C. (See the following note.) The beaker should be covered with an elevated watch glass or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85 °C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95 °C.)

11.2.4 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85 °C. *DO NOT BOIL.* This step takes about two hours for a 100 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge.)

11.2.5 Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H_2O azeotrope.)

11.2.6 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50 mL volumetric flask, make to volume with reagent water, stopper and mix.

11.2.7 Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.3 Solid Sample Preparation—Total Recoverable Analytes

11.3.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly and transfer a portion (>20 g) to tared weighing dish, weigh the sample and record the wet weight (WW). (For samples with <35% moisture a 20 g portion is sufficient. For samples with moisture >35% a larger aliquot 50–100 g is required.) Dry the sample to a constant weight at 60 °C and record the dry weight (DW) for calculation of percent solids (Section 12.6). (The sample is dried at 60 °C to prevent the loss of mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.)

11.3.2 To achieve homogeneity, sieve the dried sample using a 5-mesh polypropylene sieve and grind in a mortar and pestle. (The sieve, mortar and pestle should be cleaned between samples.) From the dried, ground material weigh accurately a representative 1.0 ± 0.01 g aliquot (W) of the sample and transfer to a 250 mL Phillips beaker for acid extraction (Sections 1.6, 1.7, 1.8, and 1.9).

11.3.3 To the beaker add 4 mL of (1+1) HNO_3 and 10 mL of (1+4) HCl. Cover the lip of the beaker with a watch glass. Place the beaker on a hot plate for reflux extraction of the analytes. The hot plate should be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95 °C. (See the following note.)

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85 °C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95 °C.) Also, a block digester capable of maintaining a temperature of 95 °C and equipped with 250 mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step.

11.3.4 Heat the sample and gently reflux for 30 minutes. Very slight boiling may occur, however vigorous boiling must be avoided to prevent loss of the HCl-H_2O azeotrope. Some solution evaporation will occur (3–4 mL).

11.3.5 Allow the sample to cool and quantitatively transfer the extract to a 100 mL volumetric flask. Dilute to volume with reagent water, stopper and mix.

11.3.6 Allow the sample extract solution to stand overnight to separate insoluble material or centrifuge a portion of the sample solution until clear. (If after centrifuging or standing overnight the extract solution contains suspended solids that would clog the nebulizer, a portion of the extract solution may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample extract is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.4 Sample Analysis

11.4.1 Prior to daily calibration of the instrument inspect the sample introduction system including the nebulizer, torch, injector tube and uptake tubing for salt deposits, dirt and debris that would restrict solution flow and affect instrument performance. Clean the system when needed or on a daily basis.

11.4.2 Configure the instrument system to the selected power and operating conditions as determined in Sections 10.1 and 10.2.

11.4.3 The instrument must be allowed to become thermally stable before calibration and analyses. This usually requires at least 30 to 60 minutes of operation. After instrument warmup, complete any required optical profiling or alignment particular to the instrument.

11.4.4 For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures, using mixed calibration standard solutions (Section 7.9) and the calibration blank (Section 7.10.1). A peristaltic pump must be used to introduce all solutions to the nebulizer. To allow equilibrium to be reached in the plasma, aspirate all solutions for 30 seconds after reaching the plasma before beginning integration of the background corrected signal to accumulate data. When possible, use the average value of replicate integration periods of the signal to be correlated to the analyte concentration. Flush the system with the rinse blank (Section 7.10.4) for a minimum of 60 seconds (Section 4.4) between each standard. The calibration line should consist of a minimum of a calibration blank and a high standard. Replicates of the blank and highest standard provide an optimal distribution of calibration standards to minimize the confidence band for a straight-line calibration in a response region with uniform variance.[20]

11.4.5 After completion of the initial requirements of this method (Sections 10.3 and 10.4), samples should be analyzed in the same operational manner used in the calibration routine with the rinse blank also being used between all sample solutions, LFBs, LFMs, and check solutions (Section 7.10.4).

11.4.6 During the analysis of samples, the laboratory must comply with the required quality control described in Sections 9.3 and 9.4. Only for the determination of dissolved analytes or the "direct analysis" of drinking water with turbidity of <1 NTU is the sample digestion step of the LRB, LFB, and LFM not required.

11.4.7 Determined sample analyte concentrations that are 90% or more of the upper limit of the analyte LDR must be diluted with reagent water that has been acidified in the same manner as calibration blank and reanalyzed (see Section 11.4.8). Also, for the interelement spectral interference correction routines to remain valid during sample analysis, the interferant concentration must not exceed its LDR. If the interferant LDR is exceeded, sample dilution with acidified reagent water and reanalysis is required. In these circumstances analyte detection limits are raised and determination by another approved test procedure that is either more sensitive and/or interference free is recommended.

11.4.8 When it is necessary to assess an operative matrix interference (*e.g.,* signal reduction due to high dissolved solids), the tests described in Section 9.5 are recommended.

11.4.9 Report data as directed in Section 12.0.

11.5 If the method of standard additions (MSA) is used, standards are added at one or more levels to portions of a prepared sample. This technique [21] compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single-addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by the following:

$$\text{Sample Conc. (mg/L or mg/kg)} = \frac{S_2 \times V_1 \times C}{(S_1 - S_2) \times V_2}$$

Where:

C = Concentration of the standard solution (mg/L)

S_1 = Signal for fortified aliquot

S_2 = Signal for unfortified aliquot

V_1 = Volume of the standard addition (L)

V_2 = Volume of the sample aliquot (L) used for MSA

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution. An alternative to using the method of standard additions is use of the internal standard technique by adding one or more elements (not in the samples and verified not to cause an uncorrected interelement spectral interference) at the same concentration (which is sufficient for optimum precision) to the prepared samples (blanks and standards) that are affected the same as the analytes by the sample matrix. Use the ratio of analyte signal to the internal standard signal for calibration and quantitation.

12.0 Data Analysis and Calculations

12.1 Sample data should be reported in units of mg/L for aqueous samples and mg/kg dry weight for solid samples.

12.2 For dissolved aqueous analytes (Section 11.1) report the data generated directly from the instrument with allowance for sample dilution. Do not report analyte concentrations below the IDL.

12.3 For total recoverable aqueous analytes (Section 11.2), multiply solution analyte concentrations by the dilution factor 0.5, when 100 mL aliquot is used to produce the 50 mL final solution, and report data as instructed in Section 12.4. If a different aliquot volume other than 100 mL is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding 90% or more of the LDR upper limit. Do not report data below the determined analyte MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

12.4 For analytes with MDLs <0.01 mg/L, round the data values to the thousandth place and report analyte concentrations up to three significant figures. For analytes with MDLs <0.01 mg/L round the data values to the 100th place and report analyte concentrations up to three significant figures. Extract concentrations for solids data should be rounded in a similar manner before calculations in Section 12.5 are performed.

12.5 For total recoverable analytes in solid samples (Section 11.3), round the solution analyte concentrations (mg/L) as instructed in Section 12.4. Report the data up to three significant figures as mg/kg dry-weight basis unless specified otherwise by the program or data user. Calculate the concentration using the equation below:

$$\text{Sample Conc. (mg/kg) dry} - \text{weight basis} = \frac{C \times V \times D}{W}$$

Where:

C = Concentration in extract (mg/L)

V = Volume of extract (L, 100 mL = 0.1L)

D = Dilution factor (undiluted = 1)

W = Weight of sample aliquot extracted (g x 0.001 = kg)

Do not report analyte data below the estimated solids MDL or an adjusted MDL because of additional dilutions required to complete the analysis.

12.6 To report percent solids in solid samples (Section 11.3) calculate as follows:

$$\% \text{ solids (S)} = \frac{DW}{WW} \times 100$$

Where:

DW = Sample weight (g) dried at 60 °C

WW = Sample weight (g) before drying

Note: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105 °C, repeat the procedure given in Section 11.3 using a separate portion (>20 g) of the sample and dry to constant weight at 103–105 °C.

12.7 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

13.0 Method Performance

13.1 Listed in Table 4 are typical single laboratory total recoverable MDLs determined for the recommended wavelengths using simultaneous ICP–AES and the operating conditions given in Table 5. The MDLs were determined in reagent blank matrix (best case situation). PTFE beakers were used to avoid boron and silica contamination from glassware with the final dilution to 50 mL completed in polypropylene centrifuged tubes. The listed MDLs for solids are estimates and were calculated from the aqueous MDL determinations.

13.2 Data obtained from single laboratory method testing are summarized in Table 6 for five types of water samples consisting of drinking water, surface water, ground water, and two wastewater effluents. The data presented cover all analytes except cerium and titanium. Samples were prepared using the procedure described in Section 11.2. For each matrix, five replicate aliquots were prepared, analyzed and the average of the five determinations used to define the sample background concentration of each analyte. In addition, two pairs of duplicates were fortified at different concentration levels. For each method analyte, the sample background concentration, mean percent recovery, standard deviation of the percent recovery, and relative percent difference between the duplicate fortified samples are listed in Table 6. The variance of the five replicate sample background determinations is included in the calculated standard deviation of the percent recovery when the analyte concentration in the sample was greater than the MDL. The tap and well waters were processed in Teflon and quartz beakers and diluted in polypropylene centrifuged tubes. The nonuse of borosilicate glassware is reflected in the precision and recovery data for boron and silica in those two sample types.

13.3 Data obtained from single laboratory method testing are summarized in Table 7 for three solid samples consisting of EPA 884 Hazardous Soil, SRM 1645 River Sediment, and EPA 286 Electroplating Sludge. Samples were prepared using the procedure described in Section 11.3. For each method analyte, the sample background concentration, mean percent recovery of the fortified additions, the standard deviation of the percent recovery, and relative percent difference between duplicate additions were determined as described in Section 13.2. Data presented are for all analytes except cerium, silica, and titanium. Limited comparative data to other methods and SRM materials are presented in Reference 23 of Section 16.0.

13.4 Performance data for aqueous solutions independent of sample preparation from a multilaboratory study are provided in Table 8.[22]

13.5 Listed in Table 9 are regression equations for precision and bias for 25 analytes abstracted from EPA Method Study 27, a multilaboratory validation study of Method 200.7.[1] These equations were developed from data received from 12 laboratories using the total recoverable sample preparation procedure on reagent water, drinking water, surface water and three industrial effluents. For a complete review and description of the study, see Reference 16 of Section 16.0.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation (*e.g.,* Section 7.8). When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult ''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.

15.0 Waste Management

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult ''The Waste Management Manual for Laboratory Personnel'', available from the American Chemical Society at the address listed in the Section 14.2.

16.0 References

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17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 1—WAVELENGTHS, ESTIMATED INSTRUMENT DETECTION LIMITS, AND RECOMMENDED CALIBRATION

Analyte	Wavelength[a] (nm)	Estimated detection limit[b] (µg/L)	Calibrate[c] to (mg/L)
Aluminum	308.215	45	10
Antimony	206.833	32	5
Arsenic	193.759	53	10
Barium	493.409	2.3	1
Beryllium	313.042	0.27	1
Boron	249.678	5.7	1
Cadmium	226.502	3.4	2
Calcium	315.887	30	10
Cerium	413.765	48	2
Chromium	205.552	6.1	5
Cobalt	228.616	7.0	2
Copper	324.754	5.4	2
Iron	259.940	6.2	10
Lead	220.353	42	10
Lithium	670.784	[d] 3.7	5
Magnesium	279.079	30	10
Manganese	257.610	1.4	2
Mercury	194.227	2.5	2
Molybdenum	203.844	12	10
Nickel	231.604	15	2
Phosphorus	214.914	76	10
Potassium	766.491	[e] 700	20
Selenium	196.090	75	5
Silica (SiO_2)	251.611	[d] 26 (SiO_2)	10
Silver	328.068	7.0	0.5
Sodium	588.995	29	10
Strontium	421.552	0.77	1
Thallium	190.864	40	5
Tin	189.980	25	4
Titanium	334.941	3.8	10
Vanadium	292.402	7.5	2
Zinc	213.856	1.8	5

[a] The wavelengths listed are recommended because of their sensitivity and overall acceptability. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 4.1).

[b] These estimated 3-sigma instrumental detection limits [16] are provided only as a guide to instrumental limits. The method detection limits are sample dependent and may vary as the sample matrix varies. *Detection limits for solids* can be estimated by dividing these values by the grams extracted per liter, which depends upon the extraction procedure. Divide solution detection limits by 10 for 1 g extracted to 100 mL for solid detection limits.

[c] Suggested concentration for instrument calibration.[2] Other calibration limits in the linear ranges may be used.

[d] Calculated from 2-sigma data.[5]

[e] Highly dependent on operating conditions and plasma position.

TABLE 2—ON-LINE METHOD INTERELEMENT SPECTRAL INTERFERANCES ARISING FROM INTERFERANTS AT THE 100 MG/L LEVEL

Analyte	Wavelength (nm)	Interferant*
Ag	328.068	Ce, Ti, Mn
Al	308.215	V, Mo, Ce, Mn
As	193.759	V, Al, Co, Fe, Ni
B	249.678	None
Ba	493.409	None
Be	313.042	V, Ce
Ca	315.887	Co, Mo, Ce
Cd	226.502	Ni, Ti, Fe, Ce
Ce	413.765	None
Co	228.616	Ti, Ba, Cd, Ni, Cr, Mo, Ce
Cr	205.552	Be, Mo, Ni
Cu	324.754	Mo, Ti
Fe	259.940	None
Hg	194.227	V, Mo
K	766.491	None
Li	670.784	None
Mg	279.079	Ce
Mn	257.610	Ce
Mo	203.844	Ce
Na	588.995	None
Ni	231.604	Co, Tl
P	214.914	Cu, Mo
Pb	220.353	Co, Al, Ce, Cu, Ni, Ti, Fe
Sb	206.833	Cr, Mo, Sn, Ti, Ce, Fe
Se	196.099	Fe
SiO_2	251.611	None
Sn	189.980	Mo, Ti, Fe, Mn, Si
Sr	421.552	None
Tl	190.864	Ti, Mo, Co, Ce, Al, V, Mn
Ti	334.941	None
V	292.402	Mo, Ti, Cr, Fe, Ce
Zn	213.856	Ni, Cu, Fe

*These on-line interferences from method analytes and titanium only were observed using an instrument with 0.035 nm resolution (see Section 4.1.2). Interferant ranked by magnitude of intensity with the most severe interferant listed first in the row.

TABLE 3—MIXED STANDARD SOLUTIONS

Solution	Analytes
I	Ag, As, B, Ba, Ca, Cd, Cu, Mn, Sb, and Se
II	K, Li, Mo, Na, Sr, and Ti
III	Co, P, V, and Ce
IV	Al, Cr, Hg, SiO_2, Sn, and Zn
V	Be, Fe, Mg, Ni, Pb, and Tl

TABLE 4—TOTAL RECOVERABLE METHOD DETECTION LIMITS (MDL)

Analyte	MDLs Aqueous, mg/L(1)	Solids, mg/kg(2)
Ag	0.002	0.3
Al	0.02	3
As	0.008	2
B	0.003	—
Ba	0.001	0.2
Be	0.0003	0.1
Ca	0.01	2
Cd	0.001	0.2
Ce	0.02	3
Co	0.002	0.4
Cr	0.004	0.8
Cu	0.003	0.5
Fe	*0.03	6
Hg	0.007	2
K	0.3	60
Li	0.001	0.2
Mg	0.02	3
Mn	0.001	0.2
Mo	0.004	1

TABLE 4—TOTAL RECOVERABLE METHOD DETECTION LIMITS (MDL)—Continued

Analyte	MDLs Aqueous, mg/L(1)	Solids, mg/kg(2)
Na	0.03	6
Ni	0.005	1
P	0.06	12
Pb	0.01	2
Sb	0.008	2
Se	0.02	5
SiO_2	0.02	—
Sn	0.007	2
Sr	0.0003	0.1
Tl	0.001	0.2
Ti	0.02	3
V	0.003	1
Zn	0.002	0.3

(1) MDL concentrations are computed for original matrix with allowance for 2x sample preconcentration during preparation. Samples were processed in PTFE and diluted in 50-mL plastic centrifuge tubes.
(2) Estimated, calculated from aqueous MDL determinations.
— Boron not reported because of glassware contamination. Silica not determined in solid samples.
* Elevated value due to fume-hood contamination.

TABLE 5—INDUCTIVELY COUPLED PLASMA INSTRUMENT OPERATING CONDITIONS

Incident rf power	1100 watts
Reflected rf power	<5 watts
Viewing height above work coil.	15 mm
Injector tube orifice i.d.	1 mm
Argon supply	liquid argon
Argon pressure	40 psi
Coolant argon flow rate	19 L/min.
Aerosol carrier argon flow rate	620 mL/min.
Auxiliary (plasma) argon flow rate.	300 mL/min.
Sample uptake rate controlled to.	1.2 mL/min.

TABLE 6—PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES

Analyte	Sample conc. mg/L	Low spike mg/L	Average recovery R (%)	S (R)	RPD	High spike mg/L	Average recovery R (%)	S (R)	RPD
Tap Water									
Ag	<0.002	0.05	95	0.7	2.1	0.2	96	0.0	0.0
Al	0.185	0.05	98	8.8	1.7	0.2	105	3.0	3.1
As	<0.008	0.05	108	1.4	3.7	0.2	101	0.7	2.0
B	0.023	0.1	98	0.2	0.0	0.4	98	0.2	0.5
Ba	0.042	0.05	102	1.6	2.2	0.2	98	0.4	0.8
Be	<0.0003	0.01	100	0.0	0.0	0.1	99	0.0	0.0
Ca	35.2	5.0	101	8.8	1.7	20.0	103	2.0	0.9
Cd	<0.001	0.01	105	3.5	9.5	0.1	98	0.0	0.0
Co	<0.002	0.02	100	0.0	0.0	0.2	99	0.5	1.5
Cr	<0.004	0.01	110	0.0	0.0	0.1	102	0.0	0.0
Cu	<0.003	0.02	103	1.8	4.9	0.2	101	1.2	3.5
Fe	0.008	0.1	106	1.0	1.8	0.4	105	0.3	0.5
Hg	<0.007	0.05	103	0.7	1.9	0.2	100	0.4	1.0
K	1.98	5.0	109	1.4	2.3	20.	107	0.7	1.7
Li	0.006	0.02	103	6.9	3.8	0.2	110	1.9	4.4
Mg	8.08	5.0	104	2.2	1.5	20.0	100	0.7	1.1
Mn	<0.001	0.01	100	0.0	0.0	0.1	99	0.0	0.0
Mo	<0.004	0.02	95	3.5	10.5	0.2	108	0.5	1.4
Na	10.3	5.0	99	3.0	2.0	20.0	106	1.0	1.6
Ni	<0.005	0.02	108	1.8	4.7	0.2	104	1.1	2.9
P	0.045	0.1	102	13.1	9.4	0.4	104	3.2	1.3
Pb	<0.01	0.05	95	0.7	2.1	0.2	100	0.2	0.5
Sb	<0.008	0.05	99	0.7	2.0	0.2	102	0.7	2.0
Se	<0.02	0.1	87	1.1	3.5	0.4	99	0.8	2.3
SiO_2	6.5	5.0	104	3.3	3.4	20.0	96	1.1	2.3
Sn	<0.007	0.05	103	2.1	5.8	0.2	101	1.8	5.0
Sr	0.181	0.1	102	3.3	2.1	0.4	105	0.8	1.0
Tl	<0.02	0.1	101	3.9	10.9	0.4	101	0.1	0.3
V	<0.003	0.05	101	0.7	2.0	0.2	99	0.2	0.5
Zn	0.005	0.05	101	3.7	9.0	0.2	98	0.9	2.5
Pond Water									
Ag	<0.002	0.05	92	0.0	0.0	0.2	94	0.0	0.0

TABLE 6—PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES—Continued

Analyte	Sample conc. mg/L	Low spike mg/L	Average recovery R (%)	S (R)	RPD	High spike mg/L	Average recovery R (%)	S (R)	RPD
Al	0.819	0.2	88	10.0	5.0	0.8	100	2.9	3.7
As	<0.008	0.05	102	0.0	0.0	0.2	98	1.4	4.1
B	0.034	0.1	111	8.9	6.9	0.4	103	2.0	0.0
Ba	0.029	0.05	96	0.9	0.0	0.2	97	0.3	0.5
Be	<0.0003	0.01	95	0.4	1.1	0.2	95	0.0	0.0
Ca	53.9	5.0	*	*	0.7	20.0	100	2.0	1.5
Cd	<0.001	0.01	107	0.0	0.0	0.1	97	0.0	0.0
Co	<0.002	0.02	100	2.7	7.5	0.2	97	0.7	2.1
Cr	<0.004	0.01	105	3.5	9.5	0.1	103	1.1	2.9
Cu	<0.003	0.02	98	2.1	4.4	0.2	100	0.5	1.5
Fe	0.875	0.2	95	8.9	2.8	0.8	97	3.2	3.6
Hg	<0.007	0.05	97	3.5	10.3	0.2	98	0.0	0.0
K	2.48	5.0	106	0.3	0.1	20.0	103	0.2	0.4
Li	<0.001	0.02	110	0.0	0.0	0.2	106	0.2	0.5
Mg	10.8	5.0	102	0.5	0.0	20.0	96	0.7	1.3
Mn	0.632	0.01	*	*	0.2	0.1	97	2.3	0.3
Mo	<0.004	0.02	105	3.5	9.5	0.2	103	0.4	1.0
Na	17.8	5.0	103	1.3	0.4	20.0	94	0.3	0.0
Ni	<0.005	0.02	96	5.6	9.1	0.2	100	0.7	1.5
P	0.196	0.1	91	14.7	0.3	0.4	108	3.9	1.3
Pb	<0.01	0.05	96	2.6	7.8	0.2	100	0.7	2.0
Sb	<0.008	0.05	102	2.8	7.8	0.2	104	0.4	1.0
Se	<0.02	0.1	104	2.1	5.8	0.4	103	1.6	4.4
SiO_2	7.83	5.0	151	1.6	1.3	20.0	117	0.4	0.6
Sn	<0.007	0.05	98	0.0	0.0	0.2	99	1.1	3.0
Sr	0.129	0.1	105	0.4	0.0	0.4	99	0.1	0.2
Tl	<0.02	0.1	103	1.1	2.9	0.4	97	1.3	3.9
V	0.003	0.05	94	0.4	0.0	0.2	98	0.1	0.0
Zn	0.006	0.05	97	1.6	1.8	0.2	94	0.4	0.0
Well Water									
Ag	<0.002	0.05	97	0.7	2.1	0.2	96	0.2	0.5
Al	0.036	0.05	107	7.6	10.1	0.2	101	1.1	0.8
As	<0.008	0.05	107	0.7	1.9	0.2	104	0.4	1.0
B	0.063	0.1	97	0.6	0.7	0.4	98	0.8	2.1
Ba	0.102	0.05	102	3.0	0.0	0.2	99	0.9	1.0
Be	<0.0003	0.01	100	0.0	0.0	0.1	100	0.0	0.0
Ca	93.8	5.0	*	*	2.1	20.0	100	4.1	0.1
Cd	0.002	0.01	90	0.0	0.0	0.1	96	0.0	0.0
Co	<0.002	0.02	94	0.4	1.1	0.2	94	0.4	1.1
Cr	<0.004	0.01	100	7.1	20.0	0.1	100	0.4	1.0
Cu	<0.005	0.02	100	1.1	0.4	0.2	96	0.5	1.5
Fe	0.042	0.1	99	2.3	1.4	0.4	97	1.4	3.3
Hg	<0.007	0.05	94	2.8	8.5	0.2	93	1.2	3.8
K	6.21	5.0	96	3.4	3.6	20.0	101	1.2	2.3
Li	0.001	0.02	100	7.6	9.5	0.2	104	1.0	1.9
Mg	24.5	5.0	95	5.6	0.3	20.0	93	1.6	1.2
Mn	2.76	0.01	*	*	0.4	0.1	*	*	0.7
Mo	<0.004	0.02	108	1.8	4.7	0.2	101	0.2	0.5
Na	35.0	5.0	101	11.4	0.8	20.0	100	3.1	1.5
Ni	<0.005	0.02	112	1.8	4.4	0.2	96	0.2	0.5
P	0.197	0.1	95	12.7	1.9	0.4	98	3.4	0.9
Pb	<0.01	0.05	87	4.9	16.1	0.2	95	0.2	0.5
Sb	<0.008	0.05	98	2.8	8.2	0.2	99	1.4	4.0
Se	<0.02	0.1	102	0.4	1.0	0.4	94	1.1	3.4
SiO_2	13.1	5.0	93	4.8	2.8	20.0	99	0.8	0.0
Sn	<0.007	0.05	98	2.8	8.2	0.2	94	0.2	0.5
Sr	0.274	0.1	94	5.7	2.7	0.4	95	1.7	2.2
Tl	<0.02	0.1	92	0.4	1.1	0.4	95	1.1	3.2
V	<0.003	0.05	98	0.0	0.0	0.2	99	0.4	1.0
Zn	0.538	0.05	*	*	0.7	0.2	99	2.5	1.1
Sewage Treatment Effluent									
Ag	0.009	0.05	92	1.5	3.6	0.2	95	0.1	0.0
Al	1.19	0.05	*	*	0.9	0.2	113	12.4	2.1
As	<0.008	0.05	99	2.1	6.1	0.2	93	2.1	6.5
B	0.226	0.1	217	16.3	9.5	0.4	119	13.1	20.9
Ba	0.189	0.05	90	6.8	1.7	0.2	99	1.6	0.5

TABLE 6—PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES—Continued

Analyte	Sample conc. mg/L	Low spike mg/L	Average recovery R (%)	S (R)	RPD	High spike mg/L	Average recovery R (%)	S (R)	RPD
Be	<0.0003	0.01	94	0.4	1.1	0.1	100	0.4	1.0
Ca	87.9	5.0	*	*	0.6	20.0	101	3.7	0.0
Cd	0.009	0.01	89	2.6	2.3	0.1	97	0.4	1.0
Co	0.016	0.02	95	3.1	0.0	0.2	93	0.4	0.5
Cr	0.128	0.01	*	*	1.5	0.1	97	2.4	2.7
Cu	0.174	0.02	98	33.1	4.7	0.2	98	3.0	1.4
Fe	1.28	0.1	*	*	2.8	0.4	111	7.0	0.6
Hg	<0.007	0.05	102	1.4	3.9	0.2	98	0.5	1.5
K	10.6	5.0	104	2.8	1.3	20.0	101	0.6	0.0
Li	0.011	0.02	103	8.5	3.2	0.2	105	0.8	0.5
Mg	22.7	5.0	100	4.4	0.0	20.0	92	1.1	0.2
Mn	0.199	0.01	*	*	2.0	0.1	104	1.9	0.3
Mo	0.125	0.02	110	21.2	6.8	0.2	102	1.3	0.9
Na	0.236	5.0	*	*	0.0	20.0	*	*	0.4
Ni	0.087	0.02	122	10.7	4.5	0.2	98	0.8	1.1
P	4.71	0.1	*	*	2.6	0.4	*	*	1.4
Pb	0.015	0.05	91	3.5	5.0	0.2	96	1.3	2.9
Sb	<0.008	0.05	97	0.7	2.1	0.2	103	1.1	2.9
Se	<0.02	0.1	108	3.9	10.0	0.4	101	2.6	7.2
SiO_2	16.7	5.0	124	4.0	0.9	20.0	108	1.1	0.8
Sn	0.016	0.05	90	3.8	0.0	0.2	95	1.0	0.0
Sr	0.515	0.1	103	6.4	0.5	0.4	96	1.6	0.2
Tl	<0.02	0.1	105	0.4	1.0	0.4	95	0.0	0.0
V	0.003	0.05	93	0.9	2.0	0.2	97	0.2	0.5
Zn	0.160	0.05	98	3.3	1.9	0.2	101	1.0	1.4
Industrial Effluent									
Ag	<0.0003	0.05	88	0.0	0.0	0.2	84	0.9	3.0
Al	0.054	0.05	88	11.7	12.2	0.2	90	3.9	8.1
As	<0.02	0.05	82	2.8	9.8	0.2	88	0.5	1.7
B	0.17	0.1	162	17.6	13.9	0.4	92	4.7	9.3
Ba	0.083	0.05	86	8.2	1.6	0.2	85	2.3	2.4
Be	<0.0006	0.01	94	0.4	1.1	0.1	82	1.4	4.9
Ca	500	5.0	*	*	2.8	20.0	*	*	2.3
Cd	0.008	0.01	85	4.7	6.1	0.1	82	1.4	4.4
Co	<0.004	0.02	93	1.8	5.4	0.2	83	0.4	1.2
Cr	0.165	0.01	*	*	4.5	0.1	106	6.6	5.6
Cu	0.095	0.02	93	23.3	0.9	0.2	95	2.7	2.8
Fe	0.315	0.1	88	16.4	1.0	0.4	99	6.5	8.0
Hg	<0.01	0.05	87	0.7	2.3	0.2	86	0.4	1.2
K	2.87	5.0	101	3.4	2.4	20.0	100	0.8	0.4
Li	0.069	0.02	103	24.7	5.6	0.2	104	2.5	2.2
Mg	6.84	5.0	87	3.1	0.0	20.0	87	0.9	1.2
Mn	0.141	0.01	*	*	1.2	0.1	89	6.6	4.8
Mo	1.27	0.02	*	*	0.0	0.2	100	15.0	2.7
Na	1500	5.0	*	*	2.7	20.0	*	*	2.0
Ni	0.014	0.02	98	4.4	3.0	0.2	87	0.5	1.1
P	0.326	0.1	105	16.0	4.7	0.4	97	3.9	1.4
Pb	0.251	0.05	80	19.9	1.4	0.2	88	5.0	0.9
Sb	2.81	0.05	*	*	0.4	0.2	*	*	2.0
Se	0.021	0.1	106	2.6	3.2	0.4	105	1.9	4.6
SiO_2	6.83	5.0	99	6.8	1.7	20.0	100	2.2	3.0
Sn	<0.01	0.05	87	0.7	2.3	0.2	86	0.4	1.2
Sr	6.54	0.1	*	*	2.0	0.4	*	*	2.7
Tl	<0.03	0.1	87	1.8	5.8	0.4	84	1.1	3.6
V	<0.005	0.05	90	1.4	4.4	0.2	84	1.1	3.6
Zn	0.024	0.05	89	6.0	4.4	0.2	91	3.5	8.9

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 7—PRECISION AND RECOVERY DATA IN SOLID MATRICES

Analyte	Sample conc. mg/kg	Low + spike mg/kg	Average recovery R (%)	S (R)	RPD	High + spike mg/kg	Average recovery R (%)	S (R)	RPD
EPA Hazardous Soil #884									
Ag	1.1	20	98	0.7	1.0	100	96	0.2	0.6
Al	5080	20	*	*	7.2	100	*	*	5.4
As	5.7	20	95	5.4	10.6	100	96	1.4	3.6
B	20.4	100	93	2.7	5.3	400	100	2.1	5.5
Ba	111	20	98	71.4	22.2	100	97	10.0	1.0
Be	0.66	20	97	0.7	2.3	100	99	0.1	0.2
Ca	85200	–	–	–	–	–	–	–	–
Cd	2	20	93	0.7	1.0	100	94	0.2	0.4
Co	5.5	20	96	3.5	7.7	100	93	0.8	2.1
Cr	79.7	20	87	28.8	16.5	100	104	1.3	1.1
Cu	113	20	110	16.2	4.4	100	104	4.0	4.2
Fe	16500	–	–	–	–	–	–	–	–
Hg	<1.4	10	92	2.5	7.7	40	98	0.0	0.0
K	621	500	121	1.3	0.0	2000	107	0.9	1.8
Li	6.7	10	113	3.5	4.4	40	106	0.6	0.6
Mg	24400	500	*	*	8.4	2000	*	*	10.1
Mn	343	20	*	*	8.5	100	95	11.0	1.6
Mo	5.3	20	88	5.3	13.2	100	91	1.4	4.1
Na	195	500	102	2.2	2.4	2000	100	1.5	3.7
Ni	15.6	20	100	1.8	0.0	100	94	1.5	3.6
P	595	500	106	13.4	8.0	2000	103	3.2	2.7
Pb	145	20	88	51.8	17.9	100	108	15.6	17.4
Sb	6.1	20	83	3.9	7.5	100	81	1.9	5.9
Se	<5	20	79	14.7	52.4	100	99	0.7	2.1
Sn	16.6	20	91	34.6	5.8	80	112	8.7	2.8
Sr	102	100	84	9.6	10.8	400	94	2.5	4.6
Tl	<4	20	92	4.8	14.6	100	91	1.5	4.6
V	16.7	20	104	4.2	5.4	100	99	0.8	1.7
Zn	131	20	103	31.2	7.3	100	104	7.2	6.4
EPA Electroplating Sludge #286									
Ag	6	20	96	0.2	0.4	100	93	0.1	0.4
Al	4980	20	*	*	4.4	100	*	*	5.6
As	32	20	94	1.3	0.8	100	97	0.7	1.6
B	210	100	113	2.0	1.6	400	98	1.9	3.5
Ba	39.8	20	0	6.8	0.3	100	0	1.6	5.7
Be	0.32	20	96	0.2	0.5	100	101	0.7	2.0
Ca	48500	–	–	–	–	–	–	–	–
Cd	108	20	98	2.5	0.8	100	96	0.5	0.5
Co	5.9	20	93	2.9	5.7	100	93	0.6	1.5
Cr	7580	20	*	*	0.7	100	*	*	1.3
Cu	806	20	*	*	1.5	100	94	8.3	0.7
Fe	31100	–	–	–	–	–	–	–	–
Hg	6.1	10	90	2.5	4.0	40	97	1.7	4.3
K	2390	500	75	8.3	4.0	2000	94	2.9	3.8
Li	9.1	10	101	2.8	0.5	40	106	1.6	3.1
Mg	1950	500	110	2.0	0.8	2000	108	2.3	3.2
Mn	262	20	*	*	1.8	100	91	1.2	0.9
Mo	13.2	20	92	2.1	2.9	100	92	0.3	0.0
Na	73400	500	*	*	1.7	2000	*	*	1.4
Ni	456	20	*	*	0.4	100	88	2.7	0.9
P	9610	500	*	*	2.9	2000	114	7.4	3.4
Pb	1420	20	*	*	2.1	100	*	*	1.3
Sb	<2	20	76	0.9	3.3	100	75	2.8	10.7
Se	6.3	20	86	9.0	16.6	100	103	1.6	2.7
Sn	24.0	20	87	4.0	2.7	80	92	0.7	0.0
Sr	145	100	90	8.1	8.1	400	93	2.4	4.6
Tl	16	20	89	4.6	5.3	100	92	0.8	0.9
V	21.7	20	95	1.2	1.0	100	96	0.4	0.9
Zn	12500	20	*	*	0.8	100	*	*	0.8
NBS 1645 River Sediment									
Ag	1.6	20	92	0.4	1.0	100	96	0.3	0.9
Al	5160	20	*	*	8.4	100	*	*	2.4
As	62.8	20	89	14.4	9.7	100	97	2.9	5.0
B	31.9	100	116	7.1	13.5	400	95	0.6	1.5
Ba	54.8	20	95	6.1	2.8	100	98	1.2	1.3

TABLE 7—PRECISION AND RECOVERY DATA IN SOLID MATRICES—Continued

Analyte	Sample conc. mg/kg	Low + spike mg/kg	Average recovery R (%)	S (R)	RPD	High + spike mg/kg	Average recovery R (%)	S (R)	RPD
Be	0.72	20	101	0.4	1.0	100	103	1.4	3.9
Ca	28000	–	–	–	–	–	–	–	–
Cd	9.7	20	100	1.1	0.0	100	101	0.7	1.8
Co	9.4	20	98	3.8	4.8	100	98	0.9	1.8
Cr	28500	20	*	*	0.4	100	*	*	0.7
Cu	109	20	115	8.5	0.0	100	102	1.8	1.0
Fe	84800	–	–	–	–	–	–	–	–
Hg	3.1	10	99	4.3	7.7	40	96	0.7	1.0
K	452	500	98	4.1	2.0	2000	106	1.4	2.3
Li	3.7	10	101	2.0	0.7	40	108	1.3	3.0
Mg	6360	500	*	*	1.8	2000	93	2.7	1.0
Mn	728	20	*	*	3.5	100	97	12.4	2.2
Mo	17.9	20	97	12.5	18.5	100	98	0.6	0.0
Na	1020	500	92	2.6	0.0	2000	97	1.1	1.7
Ni	36.2	20	94	5.9	4.0	100	100	1.1	1.5
P	553	500	102	1.4	0.9	2000	100	0.8	1.6
Pb	707	20	*	*	0.8	100	103	5.9	0.4
Sb	22.8	20	86	2.3	0.0	100	88	0.6	0.9
Se	6.7	20	103	14.3	27.1	100	98	3.1	7.6
Sn	309	20	*	*	1.0	80	101	7.9	2.7
Sr	782	100	91	12.3	3.0	400	96	3.3	2.6
Tl	<4	20	90	0.0	0.0	100	95	1.3	4.0
V	20.1	20	89	5.4	5.8	100	98	0.7	0.0
Zn	1640	20	*	*	1.8	100	*	*	1.1

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
– Not spiked.
+ Equivalent.

TABLE 8—ICP–AES INSTRUMENTAL PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS [a]

Element	Mean conc. (mg/L)	N [b]	RSD (%)	Accurace [c] (% of Nominal)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

[a] These performance values are independent of sample preparation because the labs analyzed portions of the same solutions using sequential or simultaneous instruments.
[b] N = Number of measurements for mean and relative standard deviation (RSD).
[c] Accuracy is expressed as a percentage of the nominal value for each analyte in the acidified, multi-element solutions.

TABLE 9—MULTILABORATORY ICP PRECISION AND ACCURACY DATA*

Analyte	Concentration µg/L	Total recoverable digestion µ/L
Aluminum	69–4792	X = 0.9380 (C) + 22.1

TABLE 9—MULTILABORATORY ICP PRECISION AND ACCURACY DATA*—Continued

Analyte	Concentration µg/L	Total recoverable digestion µ/L
Antimony	77–1406	SR = 0.0481 (X) + 18.8 0.8908 (C) + 0.9
Arsenic	69–1887	SR = 0.0682 (X) + 2.5 X = 1.0175 (C) + 3.9
Barium	9–377	SR = 0.0643 (X) + 10.3 X = 0.8.80 (C) + 1.68
Beryllium	3–1906	SR = 0.0826 (X) + 3.54 X = 1.0177 (C) − 0.55
Boron	19–5189	SR = 0.0445 (X) − 0.10 X = 0.9676 (C) + 18.7
Cadmium	9–1943	SR = 0.0743 (X) + 21.1 X = 1.0137 (C) − 0.65
Calcium	17–47170	SR = 0.0332 (X) + 0.90 X = 0.9658 (C) + 0.8
Chromium	13–1406	SR = 0.0327 (X) + 10.1 X = 1.0049 (C) − 1.2
Cobalt	17–2340	SR = 0.0571 (X) + 1.0 X = 0.9278 (C) + 1.5
Copper	8–1887	SR = 0.0407 (X) + 0.4 X = 0.9647 (C) − 3.64
Iron	13–9359	SR = 0.0406 (X) + 0.96 X = 0.9830 (C) + 5.7
Lead	42–4717	SR = 0.0790 (X) + 11.5 X = 1.0056 (C) + 4.1
Magnesium	34–13868	SR = 0.0448 (X) + 3.5 X = 0.9879 (C) + 2.2
Manganese	4–1887	SR = 0.0268 (X) + 8.1 X = 0.9725 (C) + 0.07
Molybdenum	17–1830	SR = 0.0400 (X) + 0.82 X = 0.9707 (C) − 2.3
Nickel	17–47170	SR = 0.0529 (X) + 2.1 X = 0.9869 (C) + 1.5
Potassium	347–14151	SR = 0.0393 (X) + 2.2 X = 0.9355 (C) − 183.1
Selenium	69–1415	SR = 0.0329 (X) + 60.9 X = 0.9737 (C) − 1.0
Silicon	189–9434	SR = 0.0443 (X) + 6.6 X = 0.9737 (C) − 22.6
Silver	8–189	SR = 0.2133 (X) + 22.6 X = 0.3987 (C) + 8.25
Sodium	35–47170	SR = 0.1836 (X) − 0.27 X = 1.0526 (C) + 26.7
Thallium	79–1434	SR = 0.0884 (X) + 50.5 X = 0.9238 (C) + 5.5
Vanadium	13–4698	SR = 0.0106 (X) + 48.0 X = 0.9551 (C) + 0.4
Zinc	7–7076	SR = 0.0472 (X) + 0.5 X = 0.9500 (C) + 1.82 SR = 0.0153 (X) + 7.78

*—Regression equations abstracted from Reference 16.
X = Mean Recovery, µg/L.
C = True Value for the Concentration, µg/L.
SR = Single-analyst Standard Deviation, µg/L.

BILLING CODE 6560–50–P

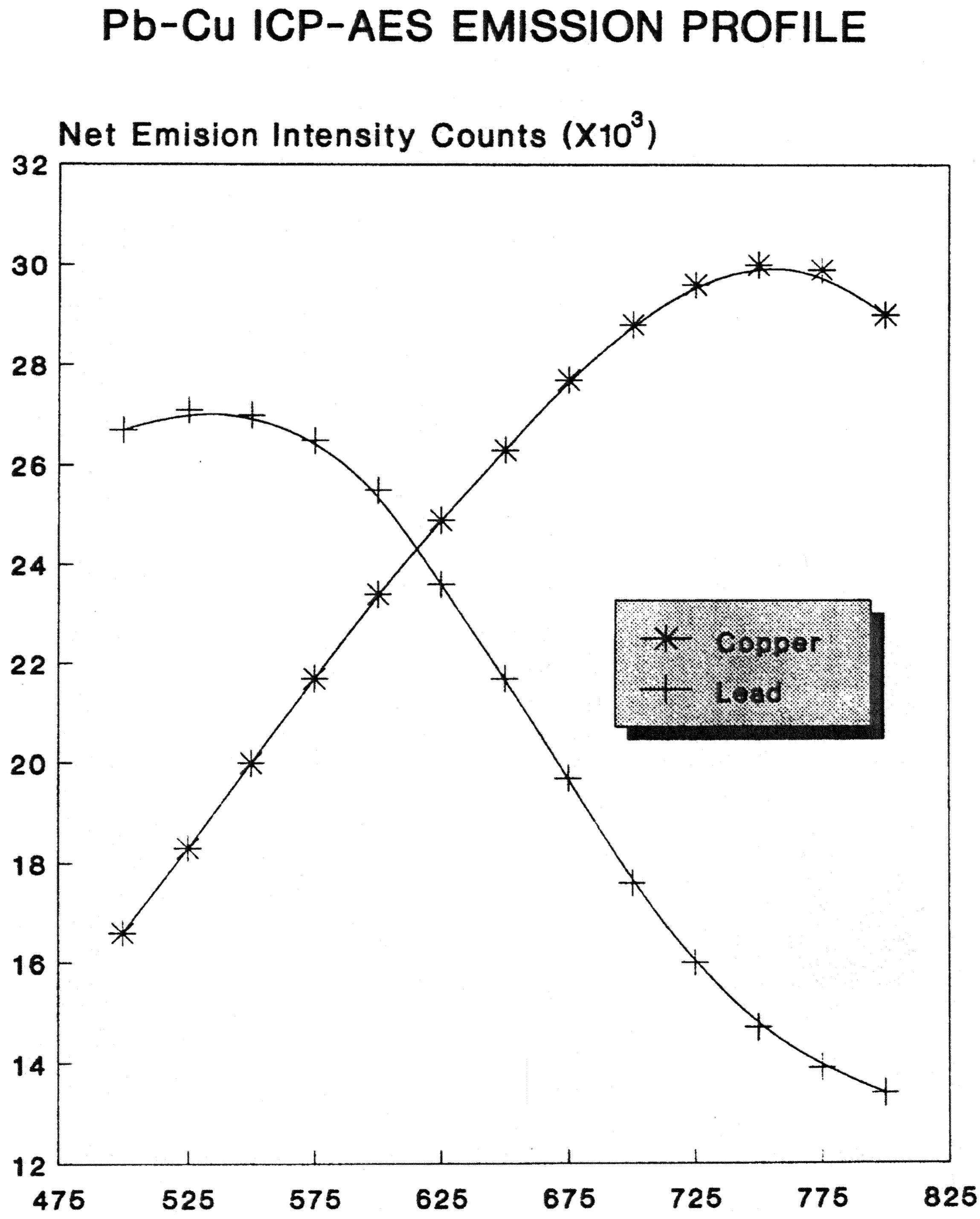

Figure 1

BILLING CODE 6560–50–C

■ 9. Revise Appendix D to Part 136 to read as follows:

Appendix D to Part 136—Precision and Recovery Statements for Methods for Measuring Metals

Two selected methods from ''Methods for Chemical Analysis of Water and Wastes,'' EPA–600/4–79–020 (1979) have been subjected to interlaboratory method validation studies. The two selected methods are for Thallium and Zinc. The following precision and recovery statements are presented in this appendix and incorporated into Part 136:

Method 279.2

For Thallium, Method 279.2 (Atomic Absorption, Furnace Technique) replace the Precision and Accuracy Section statement with the following:

Precision and Accuracy

An interlaboratory study on metal analyses by this method was conducted by the Quality Assurance Branch (QAB) of the

Environmental Monitoring Systems Laboratory—Cincinnati (EMSL–CI). Synthetic concentrates containing various levels of this element were added to reagent water, surface water, drinking water and three effluents. These samples were digested by the total digestion procedure, 4.1.3 in this manual. Results for the reagent water are given below. Results for other water types and study details are found in ''EPA Method Study 31, Trace Metals by Atomic Absorption (Furnace Techniques),'' National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161 Order No. PB 86–121 704/AS, by Copeland, F.R. and Maney, J.P., January 1986.

For a concentration range of 10.00–252 µg/L

X = 0.8781(C) − 0.715
S = 0.1112(X) + 0.669
SR = 0.1005(X) + 0.241

Where:

C = True Value for the Concentration, µg/L
X = Mean Recovery, µg/L
S = Multi-laboratory Standard Deviation, µg/L
SR = Single-analyst Standard Deviation, µg/L

Method 289.2

For Zinc, Method 289.2 (Atomic Absorption, Furnace Technique) replace the Precision and Accuracy Section statement with the following:

Precision and Accuracy

An interlaboratory study on metal analyses by this method was conducted by the Quality Assurance Branch (QAB) of the Environmental Monitoring Systems Laboratory—Cincinnati (EMSL–CI). Synthetic concentrates containing various levels of this element were added to reagent water, surface water, drinking water and three effluents. These samples were digested by the total digestion procedure, 4.1.3 in this manual. Results for the reagent water are given below. Results for other water types and study details are found in ''EPA Method Study 31, Trace Metals by Atomic Absorption (Furnace Techniques),'' National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161 Order No. PB 86–121 704/AS, by Copeland, F.R. and Maney, J.P., January 1986.

For a concentration range of 0.51–189 µg/L

X = 1.6710(C) + 1.485
S = 0.6740(X) − 0.342
SR = 0.3895(X) − 0.384

Where:

C = True Value for the Concentration, µg/L
X = Mean Recovery, µg/L
S = Multi-laboratory Standard Deviation, µg/L
SR = Single-analyst Standard Deviation, µg/L

PART 260—HAZARDOUS WASTE MANAGEMENT SYSTEM: GENERAL

■ 10. The authority citation for Part 260 continues to read as follows:

Authority: 42 U.S.C. 6905, 6912(a), 6921–6927, 6930, 6934, 6935, 6937, 6938, 6939, and 6974.

Subpart B—Definitions

■ 11. Section 260.11 is amended by revising paragraph (c)(2) to read as follows:

§ 260.11 References.

* * * * *

(c) * * *

(2) 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:

(i) Revision A, EPA–821–R–98–002, February 1999, IBR approved for Part 261, Appendix IX.

(ii) Revision B, EPA–821–R–10–001, February 2010, IBR approved for Part 261, Appendix IX.

* * * * *

PART 423—STEAM ELECTRIC POWER GENERATING POINT SOURCE CATEGORY

■ 12. The authority citation for Part 423 continues to read as follows:

Authority: Secs. 301; 304(b), (c), (e), and (g); 306(b) and (c); 307(b) and (c); and 501, Clean Water Act (Federal Water Pollution Control Act Amendments of 1972, as amended by Clean Water Act of 1977) (the ''Act''; 33 U.S.C. 1311; 1314(b), (c), (e), and (g); 1316(b) and (c); 1317(b) and (c); and 1361; 86 Stat. 816, Pub. L. 92–500; 91 Stat. 1567, Pub. L. 95–217), unless otherwise noted.

■ 13. Section 423.11 is amended by revising paragraphs (a) and (l) to read as follows:

§ 423.11 Specialized definitions.

* * * * *

(a) The term *total residual chlorine* (or total residual oxidants for intake water with bromides) means the value obtained using any of the ''chlorine—total residual'' methods in Table IB in 40 CFR 136.3(a), or other methods approved by the permitting authority.

* * * * *

(l) The term *free available chlorine* means the value obtained using any of the ''chlorine—free available'' methods in Table IB in 40 CFR 136.3(a) where the method has the capability of measuring free available chlorine, or other methods approved by the permitting authority.

* * * * *

PART 430—PULP, PAPER, AND PAPERBOARD POINT SOURCE CATEGORY

■ 14. The authority citation for Part 430 continues to read as follows:

Authority: Secs. 301, 304, 306, 307, 308, 402, and 501, Clean Water Act as amended, (33 U.S.C. 1311, 1314, 1316, 1317, 1318, 1342, and 1361) and Section 112 of the Clean Air Act, as amended (42 U.S.C. 7412).

■ 15. Section 430.01 is amended by revising paragraph (a) and by adding paragraphs (s) through (v) to read as follows:

§ 430.01 General definitions.

* * * * *

(a) *Adsorbable organic halides (AOX).* A bulk parameter that measures the total mass of chlorinated organic matter in water and wastewater. The approved method of analysis for AOX is Method 1650, which is available in Appendix A of this part, and online at *http://water.epa.gov/scitech/methods/cwa/index.cfm.*

* * * * *

(s) TCDD. 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. The approved method of analysis for TCDD is Method 1613B, which is available in Appendix A of this part, and online at *http://water.epa.gov/scitech/methods/cwa/index.cfm.*

(t) TCDF. 2,3,7,8-tetrachlorodibenzofuran. The approved method of analysis for TCDF is Method 1613B, which is available in Appendix A of this part, and online at *http://water.epa.gov/scitech/methods/cwa/index.cfm.*

(u) Chloroform. The approved methods of analysis for chloroform are listed in Table IC at 40 CFR 136.3.

(v) The approved method of analysis for the following chlorinated phenolic compounds is Method 1653, which is available in Appendix A of this part, and online at *http://water.epa.gov/scitech/methods/cwa/index.cfm*:

(1) Trichlorosyringol.
(2) 3,4,5-Trichlorocatechol.
(3) 3,4,6-Trichlorocatechol.
(4) 3,4,5-Trichloroguaiacol.
(5) 3,4,6-Trichloroguaiacol.
(6) 4,5,6-Trichloroguaiacol.
(7) 2,4,5-Trichlorophenol.
(8) 2,4,6-Trichlorophenol.
(9) Tetrachlorocatechol.
(10) Tetrachloroguaiacol.
(11) 2,3,4,6–Tetrachlorophenol.
(12) Pentachlorophenol.

PART 435—OIL AND GAS EXTRACTION POINT SOURCE CATEGORY

■ 16. The authority citation for part 435 continues to read as follows:

Authority: 33 U.S.C. 1311, 1314, 1316, 1317, 1318, 1342, and 1361.

■ 17. Section 435.11 is amended as follows:

■ a. By revising paragraph (d).
■ b. By revising paragraph (e).
■ c. By revising paragraph (k)(2).

■ d. By revising paragraph (o).
■ e. By revising paragraph (t).
■ f. By revising paragraph (u).
■ g. By revising paragraph (v).
■ h. By revising paragraph (x).
■ i. By revising paragraph (ee).
■ j. By revising paragraph (gg).
■ k. By revising paragraph (hh).
■ l. By revising paragraph (ss).
■ m. By adding paragraph (uu).

§ 435.11 Special definitions.

* * * * *

(d) *Base fluid retained on cuttings* as applied to BAT effluent limitations and NSPS refers to the ''Determination of the Amount of Non-Aqueous Drilling Fluid (NAF) Base Fluid from Drill Cuttings by a Retort Chamber (Derived from API Recommended Practice 13B–2)'', EPA Method 1674, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(e) *Biodegradation rate* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to the ''Protocol for the Determination of Degradation of Non Aqueous Base Fluids in a Marine Closed Bottle Biodegradation Test System: Modified ISO 11734:1995,'' EPA Method 1647, supplemented with ''Procedure for Mixing Base Fluids With Sediments,'' EPA Method 1646. Both EPA Method 1646 and 1647 are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

* * * * *

(k) * * *

(2) *Dry drill cuttings* means the residue remaining in the retort vessel after completing the retort procedure specified in EPA Method 1674, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

* * * * *

(o) *Formation oil* means the oil from a producing formation which is detected in the drilling fluid, as determined by the GC/MS compliance assurance method, EPA Method 1655, when the drilling fluid is analyzed before being shipped offshore, and as determined by the RPE method, EPA Method 1670, when the drilling fluid is analyzed at the offshore point of discharge. The GC/MS compliance assurance method and the RPE method approved for use with this part are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section. Detection of formation oil by the RPE method may be confirmed by the GC/MS compliance assurance method, and the results of the GC/MS compliance assurance method shall apply instead of those of the RPE method.

* * * * *

(t) *Maximum weighted mass ratio averaged over all NAF well sections* for BAT effluent limitations and NSPS for base fluid retained on cuttings means the weighted average base fluid retention for all NAF well sections as determined by EPA Method 1674, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(u) *Method 1654A* refers to EPA Method 1654, Revision A, entitled ''PAH Content of Oil by HPLC/UV,'' December 1992, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(v) *Minimum* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings means the minimum 96-hour LC_{50} value allowed as measured in any single sample of the discharged waste stream. *Minimum* as applied to BPT and BCT effluent limitations and NSPS for sanitary wastes means the minimum concentration value allowed as measured in any single sample of the discharged waste stream.

* * * * *

(x) *No discharge of free oil* means that waste streams may not be discharged that contain free oil as evidenced by the monitoring method specified for that particular stream, *e.g.,* deck drainage or miscellaneous discharges cannot be discharged when they would cause a film or sheen upon or discoloration of the surface of the receiving water; drilling fluids or cuttings may not be discharged when they fail EPA Method 1617 (Static Sheen Test), which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

* * * * *

(ee) *Sediment toxicity* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' and sediment preparation procedures specified in EPA Method 1646. EPA Method 1644 is published in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' (see paragraph (uu) of this section) and EPA Method 1646 is published as an appendix to Subpart A of this part.

* * * * *

(gg) *SPP toxicity* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to the bioassay test procedure, ''Suspended Particulate Phase (SPP) Toxicity Test,'' presented in EPA Method 1619, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(hh) *Static sheen test* means the standard test procedure that has been developed for this industrial subcategory for the purpose of demonstrating compliance with the requirement of no discharge of free oil. The methodology for performing the static sheen test is presented in EPA Method 1617, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

* * * * *

(ss) *C_{16}-C_{18} internal olefin drilling fluid* means a C_{16}-C_{18} internal olefin drilling fluid formulated as specified in appendix 1 of subpart A of this part.

* * * * *

(uu) *Analytic Methods for the Oil and Gas Extraction Point Source Category* is the EPA document, ''Analytic Methods for the Oil and Gas Point Source Category,'' December 2011, EPA–821–R–11–004, that compiles analytic methods for this category. This incorporation by reference was approved by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be inspected 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: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html*. A copy may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460. This method may be obtained at *http://water.epa.gov/scitech/methods/cwa/index.cfm*.

■ 18. In § 435.12, Footnote 1 to the table is revised to read as follows:

§ 435.12 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

* * * * *

[1] No discharge of free oil. See § 435.11(x).

* * * * *

■ 19. In § 435.13:

■ a. Remove ''LC_5'' and add in its place ''LC_{50}'' wherever it appears.

■ b. Footnotes 2, 3, and 5 through 11 to the table are revised to read as follows:

§ 435.13 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable (BAT).

* * * * *

[2] As determined by the suspended particulate phase (SPP) toxicity test. See § 435.11(gg).

[3] As determined by the static sheen test. See § 435.11(hh).

* * * * *

[5] PAH mass ratio = Mass (g) of PAH (as phenanthrene)/Mass (g) of stock base fluid as determined by EPA Method 1654, Revision A, [specified at § 435.11(u)] entitled ''PAH Content of Oil by HPLC/UV,'' December 1992, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu).

[6] Base fluid sediment toxicity ratio = 10-day LC_{50} of C_{16}-C_{18} internal olefin/10-day LC_{50} of stock base fluid as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after preparing the sediment according to the procedure specified in EPA Method 1646, which are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu).

[7] Biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{16}-C_{18} internal olefin/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(e) and (uu).

[8] Drilling fluid sediment toxicity ratio = 4-day LC_{50} of C_{16}-C_{18} internal olefin drilling fluid/4-day LC_{50} of drilling fluid removed from drill cuttings at the solids control equipment as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu).

[9] As determined before drilling fluids are shipped offshore by the GC/MS compliance assurance method (EPA Method 1655), and as determined prior to discharge by the RPE method (EPA Method 1670) applied to drilling fluid removed from drill cuttings. If the operator wishes to confirm the results of the RPE method (EPA Method 1670), the operator may use the GC/MS compliance assurance method (EPA Method 1655). Results from the GC/MS compliance assurance method (EPA Method 1655) shall supersede the results of the RPE method (EPA Method 1670). EPA Method 1655 and 1670 are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu).

[10] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings averaged over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the base fluid sediment toxicity ratio (Footnote 6), biodegradation rate ratio (Footnote 7), PAH, mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

[11] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings average over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the ester base fluid sediment toxicity ratio and ester biodegradation rate ratio stock limitations defined as:

(a) ester base fluid sediment toxicity ratio = 10-day LC_{50} of C_{12}-C_{14} ester or C_8 ester/10-day LC_{50} of stock base fluid as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu);

(b) ester biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{12}-C_{14} ester or C_8 ester/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(e) and (uu); and

(c) PAH mass ratio (Footnote 5), mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

■ 20. In § 435.14 footnote 2 to the table is revised to read as follows:

§ 435.14 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best conventional pollutant control technology (BCT).

* * * * *

[2] As determined by the static sheen test. See § 435.11(hh).

* * * * *

■ 21. In § 435.15:

■ a. Remove ''LC_5'' and add in its place ''LC_{50}''wherever it appears.

■ b. Footnotes 2, 3, and 5 through 11 to the table are revised to read as follows:

§ 435.15 Standards of performance for new sources (NSPS).

* * * * *

[2] As determined by the suspended particulate phase (SPP) toxicity test. See § 435.11(gg).

[3] As determined by the static sheen test. See § 435.11(hh).

* * * * *

[5] PAH mass ratio = Mass (g) of PAH (as phenanthrene)/Mass (g) of stock base fluid as determined by EPA Method 1654, Revision A, [specified at § 435.11(u)] entitled ''PAH Content of Oil by HPLC/UV,'' December 1992, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu).

[6] Base fluid sediment toxicity ratio = 10-day LC_{50} of C_{16}-C_{18} internal olefin/10-day LC_{50} of stock base fluid as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after preparing the sediment according to the procedure specified in EPA Method 1646, which are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu).

[7] Biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{16}-C_{18} internal olefin/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(e) and (uu).

[8] Drilling fluid sediment toxicity ratio = 4-day LC_{50} of C_{16}-C_{18} internal olefin drilling fluid/4-day LC_{50} of drilling fluid removed from drill cuttings at the solids control equipment as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after sediment preparation procedures specified in

EPA Method 1646, which are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu).

[9] As determined before drilling fluids are shipped offshore by the GC/MS compliance assurance method (EPA Method 1655), and as determined prior to discharge by the RPE method (EPA Method 1670) applied to drilling fluid removed from drill cuttings. If the operator wishes to confirm the results of the RPE method (EPA Method 1670), the operator may use the GC/MS compliance assurance method (EPA Method 1655). Results from the GC/MS compliance assurance method (EPA Method 1655) shall supersede the results of the RPE method (EPA Method 1670). EPA Method 1655 and 1670 are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu).

[10] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings averaged over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the base fluid sediment toxicity ratio (Footnote 6), biodegradation rate ratio (Footnote 7), PAH, mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

[11] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings average over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the ester base fluid sediment toxicity ratio and ester biodegradation rate ratio stock limitations defined as:

(a) ester base fluid sediment toxicity ratio = 10-day LC_{50} of C_{12}-C_{14} ester or C_8 ester/10-day LC_{50} of stock base fluid as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu);

(b) ester biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{12}-C_{14} ester or C_8 ester/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(e) and (uu); and

(c) PAH mass ratio (Footnote 5), mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

■ 22. The heading of Appendix 1 to Subpart A of Part 435 is revised to read as follows:

Appendix 1 to Subpart A of Part 435—Static Sheen Test (EPA Method 1617)

* * * * *

■ 23. Appendix 2 to Subpart A of Part 435 is amended as follows:

■ a. Revise the appendix heading.

■ b. Remove the fourth sentence from Section II.C.6.

■ c. Revise Section III.A.1.

■ d. Revise Section III.E.2.

The revisions read as follows:

Appendix 2 to Subpart A of Part 435—Drilling Fluids Toxicity Test (EPA Method 1619)

* * * * *

III–A. * * *

(1) Each definitive test consists of 18 test containers: 3 replicates of a control and 5 SPP dilutions. Test containers should be Pyrex or equivalent glass. For definitive tests, 5 SPP dilutions with 3 replicates of at least 500 ml each are required. Twenty mysids per replicate, 360 per definitive test are required.

* * * * *

III–E. * * *

(2) Establish the definitive test concentrations based on results of a range finding test or based on prior experience and knowledge of the mud system.

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■ 24. The heading of Appendix 3 to Subpart A of Part 435 is amended to read as follows:

Appendix 3 to Subpart A of Part 435—Procedure for Mixing Base Fluids With Sediments (EPA Method 1646)

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■ 25. Appendix 4 to Subpart A of Part 435 is revised to read as follows:

Appendix 4 to Subpart A of Part 435—Protocol for the Determination of Degradation of Non-Aqueous Base Fluids in a Marine Closed Bottle Biodegradation Test System: Modified ISO 11734:1995 (EPA Method 1647)

1.0. Summary of EPA Method 1647

a. This method determines the anaerobic degradation potential of mineral oils, paraffin oils and non-aqueous fluids (NAF) in sediments. These substrates are base fluids for formulating offshore drilling fluids. The test evaluates base fluid biodegradation rates by monitoring gas production due to microbial degradation of the test fluid in natural marine sediment.

b. The test procedure places a mixture of marine/estuarine sediment, test substrate (hydrocarbon or controls) and seawater into clean 120 mL (150 mL actual volume) Wheaton serum bottles. The test is run using four replicate serum bottles containing 2,000 mg carbon/kg dry weight concentration of test substrate in sediment. The use of resazurin dye solution (1 ppm) evaluates the anaerobic (redox) condition of the bottles (dye is blue when oxygen is present, reddish in low oxygen conditions and colorless if oxygen free). After capping the bottles, a nitrogen sparge removes air in the headspace before incubation begins. During the incubation period, the sample should be kept at a constant temperature of 29 ± 1°C. Gas production and composition is measured approximately every two weeks. The samples need to be brought to ambient temperature before making the measurements. Measure gas production using a pressure gauge. Barometric pressure is measured at the time of testing to make necessary volume adjustments.

c. ISO 11734:1995 specifies that total gas is the standard measure of biodegradation. While modifying this test for evaluating biodegradation of NAFs, methane was also monitored and found to be an acceptable method of evaluating biodegradation. Section 7 contains the procedures used to follow biodegradation by methane production. Measurement of either total gas or methane production is permitted. If methane is followed, determine the composition of the gas by using gas chromatography (GC) analysis at each sampling. At the end of the test when gas production stops, or at around 275 days, an analysis of sediment for substrate content is possible. Common methods which have been successfully used for analyzing NAFs from sediments are listed in Section 8.

2.0 System Requirements

This environmental test system has three phases, spiked sediment, overlying seawater, and a gas headspace. The sediment/test compound mixture is combined with synthetic sea water and transferred into 120-mL serum bottles. The total volume of sediment/sea water mixture in the bottles is 75 mL. The volume of the sediment layer will be approximately 50 mL, but the exact volume of the sediment will depend on sediment characteristics (wet:dry ratio and density). The amount of synthetic sea water will be calculated to bring the total volume in the bottles to 75 mL. The test systems are maintained at a temperature of 29 ± 1°C during incubation. The test systems are brought to ambient temperatures prior to measuring pressure or gas volume.

2.1 Sample Requirements

a. The concentration of base fluids are at least 2,000 mg carbon test material/kg dry sediment. Carbon concentration is determined by theoretical composition based on the chemical formula or by chemical analysis by ASTM D5291–96. Sediments with positive, intermediate and negative control substances as well as a C_{16}-C_{18} internal olefin type base fluid will be run in conjunction with test materials under the same conditions. The positive control is ethyl oleate (CAS 111–62–6), the intermediate control is 1-hexadecene (CAS 629–73–2), and the negative control is squalane (CAS 111–01–3). Controls must be of analytical grade or the highest grade available. Each test control concentration should be prepared according to the mixing procedure described in Section 3.1.

b. Product names will be used for examples or clarification in the following text. Any use of trade or product names in this publication is for descriptive use only, and does not constitute endorsement by EPA or the authors.

2.2. Seawater Requirements

Synthetic seawater at a salinity of 25 ± 1 ppt should be used for the test. The synthetic seawater should be prepared by mixing a commercially available artificial seawater mix, into high purity distilled or de-ionized water. The seawater should be aerated and allowed to age for approximately one month prior to use.

2.3. Sediment Requirements

a. The dilution sediment must be from a natural estuarine or marine environment and be free of the compounds of interest. The collection location, date and time will be documented and reported. The sediment is prepared by press-sieving through a 2,000-micron mesh sieve to remove large debris, then press-sieving through a 500-micron sieve to remove indigenous organisms that may confound test results. The water content of the sediment should be less than 60% (w/w) or a wet to dry ratio of 2.5. The sediment should have a minimum organic matter content of 3% (w/w) as determined by ASTM D2974–07a (Method A and D and calculate organic matter as in Section 8.3 of method ASTM D2974–07a).

b. To reduce the osmotic shock to the microorganisms in the sediment the salinity of the sediment's pore water should be between 20–30 ppt. Sediment should be used for testing as soon as possible after field collection. If required, sediment can be stored in the dark at 4 °C with 3–6 inches of overlying water in a sealed container for a maximum period of 2 months prior to use.

3.0 Test Set Up

The test is set up by first mixing the test or control substrates into the sediment inoculum, then mixing in seawater to make a pourable slurry. The slurry is then poured into serum bottles, which are then flushed with nitrogen and sealed.

3.1. Mixing Procedure

Because base fluids are strongly hydrophobic and do not readily mix with sediments, care must be taken to ensure base fluids are thoroughly homogenized within the sediment. All concentrations are weight-to-weight comparisons (mg of base fluid to kg of dry control sediment). Sediment and base fluid mixing will be accomplished by using the following method.

3.1.1. Determine the wet to dry weight ratio for the control sediment by weighing approximately 10 sub-samples of approximately 1 g each of the screened and homogenized wet sediment into tared aluminum weigh pans. Dry sediment at 105 °C for 18–24 h. Remove the dried sediments and cool in a desiccator. Repeat the drying, cooling, and weighing cycle until a constant weight is achieved (within 4% of previous weight). Re-weigh the samples to determine the dry weight. Calculate the mean wet and dry weights of the 10 sub samples and determine the wet/dry ratio by dividing the mean wet weight by the mean dry weight using Equation 5–1. This is required to determine the weight of wet sediment needed to prepare the test samples.

$$\frac{\text{Mean Wet Sediment Weight (g)}}{\text{Mean Dry Sediment Weight (g)}} = \text{Wet to Dry Ratio} \qquad \text{[Eq.1]}$$

3.1.2. Determine the density (g/ml) of the wet sediment. This will be used to determine total volume of wet sediment needed for the various test treatments. One method is to tare a 5 ml graduated cylinder and add about 5 ml of homogenized sediment. Carefully record the volume then weigh this volume of sediment. Repeat this a total of three times. To determine the wet sediment density, divide the weight by volume per the following formula:

$$\frac{\text{Mean Wet Sediment Weight (g)}}{\text{Mean Wet Sediment Volume (mL)}} = \text{Wet Sediment Density (g/mL)} \qquad \text{[Eq. 2]}$$

3.1.3. Determine the amount of base fluid to be spiked into wet sediment in order to obtain the desired initial base fluid concentration of 2,000 mg carbon/kg dry weight. An amount of wet sediment that is the equivalent of 30 g of dry sediment will be added to each bottle. A typical procedure is to prepare enough sediment for 8 serum bottles (3 bottles to be sacrificed at the start of the test, 4 bottles incubated for headspace analysis, and enough extra sediment for 2 extra bottles). Extra sediment is needed because some of the sediment will remain coated onto the mixing bowl and utensils. Experience with this test may indicate that preparing larger volumes of spiked sediment is a useful practice, then the following calculations should be adjusted accordingly.

a. Determine the total weight of dry sediment needed to add 30 g dry sediment to 8 bottles. If more bottles are used then the calculations should be modified accordingly. For example:

$$\text{30 g dry sediment per bottle} \times 8 = \text{240 g dry sediment} \qquad \text{[Eq.3]}$$

b. Determine the weight of base fluid, in terms of carbon, needed to obtain a final base fluid concentration of 2,000 mg carbon/kg dry weight. For example:

$$\frac{\text{2,000 mg carbon}}{\text{Per kg dry sediment}} \times \frac{\text{240 g}}{\text{1,000}} = \text{480 mg carbon} \qquad \text{[Eq. 4]}$$

c. i. Convert from mg of carbon to mg of base fluid. This calculation will depend on the % fraction of carbon present in the molecular structure of each base fluid. For the control fluids, ethyl oleate is composed of 77.3% carbon, hexadecene is composed of 85.7% carbon, and squalane is composed of 85.3% carbon. The carbon fraction of each base fluid should be supplied by the manufacturer or determined before use. ASTM D5291–96 or equivalent will be used to determine composition of fluid.

ii. To calculate the amount of base fluid to add to the sediment, divide the amount of carbon (480 mg) by the percent fraction of carbon in the fluid.

iii. For example, the amount of ethyl oleate added to 240 g dry weight sediment can be calculated from the following equation:

$$\frac{480 \text{ mg carbon}}{(77.3 \div 100)} = 621 \text{ mg ethyl oleate} \qquad \text{[Eq. 5]}$$

iv. Therefore, add 621 mg of ethyl oleate to 240 g dry weight sediment for a final concentration of 2,000 mg carbon/kg sediment dry weight.

3.1.4. Mix the calculated amount of base fluid with the appropriate weight of wet sediment.

a. Use the wet:dry ratio to convert from g sediment dry weight to g sediment wet weight, as follows:

$$240 \text{ g dry sediment} \times \text{wet:dry ratio} = \text{g wet sediment needed} \qquad \text{[Eq. 6]}$$

b. i. Weigh the appropriate amount of base fluid (calculated in Section 3.1.3.c) into stainless mixing bowls, tare the vessel weight, then add the wet sediment calculated in Equation 5, and mix with a high shear dispersing impeller for 9 minutes.

ii. The sediment is now mixed with synthetic sea water to form a slurry that will be transferred into the bottles.

3.2. Creating Seawater/Sediment Slurry

Given that the total volume of sediment/sea water slurry in each bottle is to be 75 mL, determine the volume of sea water to add to the wet sediment.

3.2.1. If each bottle is to contain 30 g dry sediment, calculate the weight, and then the volume, of wet sediment to be added to each bottle.

$$30 \text{ g dry sediment} \times \text{wet:dry ratio} = \text{g wet sediment added to each bottle} \qquad \text{[Eq. 7]}$$

$$\frac{\text{g wet sediment}}{\text{Density (g/mL) of wet sediment}} = \text{mL wet sediment} \qquad \text{[Eq. 8]}$$

3.2.2. Calculate volume of sea water to be added to each bottle.

$$75 \text{ mL total volume} - \text{mL wet sediment (from Eq. 8)} = \text{mL of sea water} \qquad \text{[Eq. 9]}$$

3.2.3. Determine the ratio of sea water to wet sediment (volume:volume) in each bottle.

$$\frac{\text{Volume sea water per bottle (Eq. 9)}}{\text{Volume sediment water per bottle (Eq. 8)}} = \text{Ratio of sea water:wet sediment} \qquad \text{[Eq. 10]}$$

3.2.4. Convert the wet sediment weight from Equation 6 into a volume using the sediment density.

$$\text{g wet sediment (Eq. 6) density} = \text{volume (mL) of sediment} \qquad \text{[Eq. 11]}$$

3.2.5. Determine the amount of sea water to mix with the wet sediment.

$$\underset{\text{(Eq. 11)}}{\text{mL wet sediment}} \times \underset{\text{(Eq. 10)}}{\text{Sea water:sediment ratio}} = \text{mL sea water to add to wet sediment} \qquad \text{[Eq. 12]}$$

Mix sea water thoroughly with wet sediment to form a sediment/sea water slurry.

3.3. Bottling the Sediment Seawater Slurry

The total volume of sediment/sea water slurry in each bottle is to be 75 mL. Convert the volume (mL) of sediment/sea water slurry into a weight (g) using the density of the sediment and the seawater.

3.3.1. Determine the weight of sediment to be added to each bottle.

$$\text{mL sediment (Eq. 8)} \times \text{density of wet sediment (g/mL)} = \text{g wet sediment} \quad \text{[Eq. 13]}$$

3.3.2. Determine the weight of sea water to be added to each bottle.

$$\text{mL sea water (Eq. 9)} \times \text{density of sea water (1.01 g/mL)} = \text{g sea water} \quad \text{[Eq. 14]}$$

3.3.3. Determine weight of sediment/sea water slurry to be added to each bottle.

$$\text{g wet sediment (Eq. 13)} + \text{g sea water (Eq. 14)} = \text{g sediment/sea water slurry} \quad \text{[Eq. 15]}$$

This should provide each bottle with 30 g dry sediment in a total volume of 75 mL.

3.3.4. Putting the sediment:seawater slurry in the serum bottles.

a. **Note:** The slurry will need to be constantly stirred to keep the sediment suspended.

b. Place a tared serum bottle on a balance and add the appropriate amount of slurry to the bottle using a funnel. Once the required slurry is in the bottle remove the funnel, add 2–3 drops (25 µL) of a 1 gram/L resazurin dye stock solution. Cap the bottle with a butyl rubber stopper (Bellco Glass, Part #2048–11800) and crimp with an aluminum seal (Bellco Glass Part #2048–11020).

c. Using a plastic tube with a (23-gauge, 1-inch long) needle attached to one side and a nitrogen source to the other, puncture the serum cap with the needle. Puncture the serum cap again with a second needle to sparge the bottle's headspace of residual air for two minutes. The nitrogen should be flowing at no more than 100 mL/min to encourage gentle displacement of oxygenated air with nitrogen. Faster nitrogen flow rates would cause mixing and complete oxygen removal would take much longer. Remove the nitrogen needle first to avoid any initial pressure problems. The second (vent) needle should be removed within 30 seconds of removing the nitrogen needle.

d. Triplicate blank test systems are prepared, with similar quantities of sediment and seawater without any base fluid. Incubate in the dark at a constant temperature of 29 ± 1 °C.

e. Record the test temperature. The test duration is dependent on base fluid performance, but at a maximum should be no more than 275 days. Stop the test after all base fluids have achieved a plateau of gas production. At termination, base fluid concentrations can be verified in the terminated samples by extraction and GC analysis according to Section 8.

4.0. Concentration Verification Chemical Analyses

a. Because of the difficulty of homogeneously mixing base fluid with sediment, it is important to demonstrate that the base fluid is evenly mixed within the sediment sea water slurry that was added to each bottle. Of the seven serum bottles set up for each test or control condition, three are randomly selected for concentration verification analyses. These should be immediately placed at 4 °C and a sample of sediment from each bottle should be analyzed for base fluid content as soon as possible. The coefficient of variation (CV) for the replicate samples must be less than 20%. The results should show recovery of at least 70% of the spiked base fluid. Use an appropriate analytical procedure described in Section 8 to perform the extractions and analyses. If any set of sediments fail the criteria for concentration verification, then the corrective action for that set of sediments is also outlined in Section 8.

b. The nominal concentrations and the measured concentrations from the three bottles selected for concentration verification should be reported for the initial test concentrations. The coefficient of variation (CV) for the replicate samples must be less than 20%. If base fluid content results are not within the 20% CV limit, the test must be stopped and restarted with adequately mixed sediment.

5.0. Gas Monitoring Procedures

Biodegradation is measured by total gas as specified in ISO 11734:1995. Methane production can also be tracked and is described in Section 7.

5.1. Total Gas Monitoring Procedures

Bottles should be brought to room temperature before readings are taken. a. The bottles are observed to confirm that the resazurin has not oxidized to pink or blue. Total gas production in the culture bottles should be measured using a pressure transducer (one source is Biotech International). The pressure readings from test and control cultures are evaluated against a calibration curve created by analyzing the pressure created by known additions of gas to bottles established identically to the culture bottles. Bottles used for the standard curve contain 75 mL of water, and are sealed with the same rubber septa and crimp cap seals used for the bottles containing sediment. After the bottles used in the standard curve have been sealed, a syringe needle inserted through the septa is used to equilibrate the pressure inside the bottles to the outside atmosphere. The syringe needle is removed and known volumes of air are injected into the headspace of the bottles. Pressure readings provide a standard curve relating the volume of gas injected into the bottles and headspace pressure. No less than three points may be used to generate the standard curve. A typical standard curve may use 0, 1, 5, 10, 20 and 40 mL of gas added to the standard curve bottles.

b. The room temperature and barometric pressure (to two digits) should be recorded at the time of sampling. One option for the barometer is Fisher Part #02–400 or 02–401. Gas production by the sediment is expressed in terms of the volume (mL) of gas at standard temperature (0 °C = 273 °K) and pressure (1 atm = 30 inches of Hg) using Eq. 16.

$$V_2 = \frac{P_1 \times V_1 \times T_2}{T_1 \times P_2} \quad \text{[Eq.16]}$$

Where:

V_2 = Volume of gas production at standard temperature and pressure

P_1 = Barometric pressure on day of sampling (inches of Hg)

V_1 = Volume of gas measured on day of sampling (mL)

T_2 = Standard temperature = 273 °K

T_1 = Temperature on day of sampling (°C + 273 = °K)

P_2 = Standard pressure = 30 inches Hg

c. An estimate can be made of the total volume of anaerobic gas that will be produced in the bottles. The gas production measured for each base fluid can be expressed as a percent of predicted total anaerobic gas production.

5.1.1. Calculate the total amount of carbon in the form of the base fluid present in each bottle.

a. Each bottle is to contain 30 g dry weight sediment. The base fluid concentration is 2,000 mg carbon/kg dry weight sediment. Therefore:

$$2{,}000 \text{ mg carbon/kg sediment} \times (30 \text{ g} \div 1{,}000) = 60 \text{ mg carbon per bottle} \qquad [\text{Eq. } 17]$$

5.1.2. Theory states that anaerobic microorganisms will convert 1 mole of carbon substrate into 1 mole of total anaerobic gas production.

a. Calculate the number of moles of carbon in each bottle.

b. The molecular weight of carbon is 12 (*i.e.,* 1 mole of carbon = 12 g). Therefore, the number of moles of carbon in each bottle can be calculated.

$$\frac{60 \text{ mg carbon per bottle}/1{,}000}{12 \text{ g/mole}} = 0.005 \text{ moles carbon} \qquad [\text{Eq. } 18]$$

5.1.3. Calculate the predicted volume of anaerobic gas.

One mole of gas equals 22.4 L (at standard temperature and pressure), therefore,

$$0.005 \text{ moles} \times 22.4 \text{ L} = 0.112\text{L (or 112 mL total gas production)} \qquad [\text{Eq. } 19]$$

5.2. Gas Venting

a. If the pressure in the serum bottle is too great for the pressure transducer or syringe, some of the excess gas must be wasted. The best method to do this is to vent the excess gas right after measurement. To do this, remove the barrel from a 10-mL syringe and fill it ⅓ full with water. This is then inserted into the bottle through the stopper using a small diameter (high gauge) needle. The excess pressure is allowed to vent through the water until the bubbles stop. This allows equalization of the pressure inside the bottle to atmospheric without introducing oxygen. The amount of gas vented (which is equal to the volume determined that day) must be kept track of each time the bottles are vented. A simple way to do this in a spreadsheet format is to have a separate column in which cumulative vented gas is tabulated. Each time the volume of gas in the cultures is analyzed, the total gas produced is equal to the gas in the culture at that time plus the total of the vented gas.

b. To keep track of the methane lost in the venting procedure, multiply the amount of gas vented each time by the corrected % methane determined on that day. The answer gives the volume of methane wasted. This must be added into the cumulative totals similarly to the total gas additions.

6.0. Test Acceptability and Interpretation

6.1. Test Acceptability

At day 275 or when gas production has plateaued, whichever is first, the controls are evaluated to confirm that the test has been performed appropriately. In order for this modification of the closed bottle biodegradation test to be considered acceptable, all the controls must meet the biodegradation levels indicated in Table 1. The intermediate control hexadecene must produce at least 30% of the theoretical gas production. This level may be reexamined after two years and more data has been generated.

TABLE 1—TEST ACCEPTABILITY CRITERIA

Concentration	Percent biodegradability as a function of gas measurement		
	Positive control	Squalane negative control	Hexadecene intermediate control
2,000 mg carbon/kg	≥60% theoretical	≤5% theoretical	≥30% theoretical.

6.2 Interpretation

a. In order for a fluid to pass the closed bottle test, the biodegradation of the base fluid as indicated by the total amount of total gas (or methane) generated once gas production has plateaued (or at the end of 275 days, which ever is first) must be greater than or equal to the volume of gas (or methane) produced by the reference standard (internal elefin or ester).

b. The method for evaluating the data to determine whether a fluid has passed the biodegradation test must use the equations:

$$\frac{\%\text{ Theoretical gas production of reference fluid}}{\%\text{ Theoretical gas production of NAF}} \leq 1.0 \qquad [\text{Eq. } 20]$$

Where:

NAF = Stock base fluid being tested for compliance

Reference fluid = C_{16}-C_{18} internal olefin or C_{12} –C_{14} or C_8 ester reference fluid

7.0. Methane Measurement

7.1. Methane Monitoring Procedures

a. The use of total gas production alone may result in an underestimation of the actual metabolism occurring since CO_2 is slightly soluble in water. An acceptable alternative method is to monitor methane production and total gas production. This is easily done using GC analysis. A direct injection of headspace gases can be made into a GC using almost any packed or capillary column with an FID detector. Unless volatile fuels or solvents are present in the test material or the inocula, the only component of the headspace gas that can be detected using an FID detector is methane. The percent methane in the headspace gas is determined by comparing the response of the sample injections to the response from injections of known percent methane standards. The percent methane is corrected for water vapor saturation using Eq. 21 and then converted to a volume of dry methane using Eq. 22.

$$\text{Corrected \% CH}_4 = \frac{\text{\% CH}_4}{1 - \dfrac{D \times 22.4\ \text{L/mol}}{18\ \text{g/mol} \times 1{,}000}} \quad \text{[Eq. 21]}$$

Where:

D = The density of water vapor at saturation (g/m³, can be found in CRC Handbook of Chemistry and Physics) for the temperature of sampling.

$$V_{CH4}\ (\text{ml}) = (S + V) \times \frac{P - P_w}{T + 273} \times \frac{CH_4}{100} \times \frac{273}{760} \quad \text{[Eq. 22]}$$

Where:

V_{CH4} = Volume of methane in the bottle

S = Volume of excess gas production (measured with a pressure transducer)

V = Volume of the headspace in the culture bottle (total volume—liquid phase)

P = Barometric pressure (mm Hg, measured with barometer)

T = Temperature (°C)

P_w = Vapor pressure of water at T (mm Hg, can be found in CRC Handbook of Chemistry and Physics)

CH_4 = % methane in headspace gas (after correction for water vapor)

b. The total volume of serum bottles sold as 125 mL bottles (Wheaton) is 154.8 mL.

c. The volumes of methane produced are then compared to the volumes of methane in the controls to determine if a significant inhibition of methane production or a significant increase of methane production has been observed. Effective statistical analyses are important, as variability in the results is common due to the heterogeneity of the inoculum's source. It is also common to observe that the timing of the initiation of culture activity is not equal in all of the cultures. Expect a great variability over the period when the cultures are active, some replicates will start sooner than others, but all of the replicates should eventually reach similar levels of base fluid degradation and methane production.

7.2. Expected Methane Production Calculations

a. The amount of methane expected can be calculated using the equation of Symons and Buswell (Eq. 23). In the case of complete mineralization, all of the carbon will appear as wither CO_2 or CH_4, thus the total moles of gas produced will be equal to the total moles of carbon in the parent molecule. The use of the Buswell equation allows you to calculate the effects the redox potential will have on the distribution of the products in methanogenic cultures. More reduced electron donors will allow the production of more methane, while more oxidized electron donors will cause a production of more carbon dioxide.

$$\frac{12\ \text{mole CH}_4}{\text{mole hexadecene}} \times \frac{22.4\ \text{L}}{\text{mole CH}_4} \times \frac{1{,}000\ \text{ml}}{\text{L}} \times \frac{1\ \text{mole hexadecene}}{224.4\ \text{g hexadecene}} \times \frac{23\ \text{g hexadecene}}{\text{kg dry soil}} \times \frac{0.03\ \text{kg}}{\text{culture}} = 84\ (\text{ml}) \quad \text{[Eq. 24]}$$

b. An example calculation of the expected methane volume in a culture fed 2,000 mg/kg hexadecene is as follows. The application of Symons and Buswell's equation reveals that hexadecene ($C_{16}H_{32}$) will yield 4 moles of CO_2 and 12 moles of CH_4. Assuming 30 g of dry sediment are added to the bottles with 2,334 mg hexadecene/kg dry sediment (*i.e.,* equivalent to 2,000 mg carbon/kg dry sediment) the calculation is as follows.

$$\frac{12\ \text{mole CH}_4}{\text{mole hexadecene}} \times \frac{22.4\ \text{L}}{\text{mole CH}_4} \times \frac{1{,}000\ \text{ml}}{\text{L}} \times \frac{1\ \text{mole hexadecene}}{224.4\ \text{g hexadecene}} \times \frac{23\ \text{g hexadecene}}{\text{kg dry soil}} \times \frac{0.03\ \text{kg}}{\text{culture}} = 84\ (\text{ml}) \quad \text{[Eq. 24]}$$

c. By subtracting the average amount of methane in control bottles from the test bottles and then dividing by the expected volume an evaluation of the completion of the process may be conducted.

8.0. Concentration Verification Analysis

The Concentration Verification analysis is required at the beginning of the test to ensure homogeneity and confirm that the required amount of fluid was delivered to the sediments at the start of the test.

8.1. Three samples per fluid need to be analyzed and achieve ≤20% Coefficient of Variability and an average of ≥70% to ≤120% of fluid delivered to sediment.

8.2. If a third party performs the analysis, then the laboratory should be capable of delivering the homogeneity data within seven days, in order to identify any samples that do not meet the homogeneity requirement as quickly as possible.

8.3. If one sediment/fluid set, out a multiple set batch of samples, fails these criteria, then that one set of samples must be discarded and a fresh set of spiked sediment prepared, started, and analyzed to ensure homogeneity. The same stock sediment is used to prepare the replacement set(s). The remaining sets do not need to be re-mixed or restarted.

8.4. The re-mixed set(s) will need to be run the additional days as appropriate to ensure that the total number of days is the same for all sets of bottles, even though the specific days are not aligned.

8.5. Re-mixing of bottle sets can be performed multiple times as a result of a failure of the analytical criteria, until the holding time for the stock sediment has expired (60 days). If the problem set(s) has not fallen within the acceptable analytical criteria by then, it must not be part of the batch of bottles run. If the problem batch is one of the controls, and those controls were not successfully prepared when the sediment holding time expired, then the entire test must be restarted.

9.0 Program Quality Assurance and Quality Control

9.1 Calibration

9.1.1. All equipment/instrumentation will be calibrated in accordance with the test method or the manufacturer's instructions and may be scheduled or triggered.

9.1.2. Where possible, standards used in calibration will be traceable to a nationally recognized standard (*e.g.,* certified standard by NIST).

9.1.3. All calibration activities will be documented and the records retained.

9.1.4. The source, lot, batch number, and expiration date of all reagents used with be documented and retained.

9.2. Maintenance

9.2.1. All equipment/instrumentation will be maintained in accordance with the test method or the manufacturer's instructions and may be scheduled or triggered.

9.2.2. All maintenance activities will be documented and the records retained.

9.3. Data Management and Handling

9.3.1. All primary (raw) data will be correct, complete, without selective reporting, and will be maintained.

9.3.2. Hand-written data will be recorded in lab notebooks or electronically at the time of observation.

9.3.3. All hand-written records will be legible and amenable to reproduction by electrostatic copiers.

9.3.4. All changes to data or other records will be made by:

a. Using a single line to mark-through the erroneous entry (maintaining original data legibility).

b. Write the revision.

c. Initial, date, and provide revision code (*see* attached or laboratory's equivalent).

9.3.5. All data entry, transcriptions, and calculations will be verified by a qualified person.

a. Verification will be documented by initials of verifier and date.

9.3.6. Procedures will be in place to address data management procedures used (at minimum):

a. Significant figures.

b. Rounding practices.

c. Identification of outliers in data series.

d. Required statistics.

9.4. Document Control

9.4.1. All technical procedures, methods, work instructions, standard operating procedures must be documented and approved by laboratory management prior to the implementation.

9.4.2. All primary data will be maintained by the contractor for a minimum of five (5) years.

9.5. Personnel and Training

9.5.1. Only qualified personnel shall perform laboratory activities.

9.5.2. Records of staff training and experience will be available. This will include initial and refresher training (as appropriate).

9.6. Test Performance

9.6.1. All testing will done in accordance with the specified test methods.

9.6.2. Receipt, arrival condition, storage conditions, dispersal, and accountability of the test article will be documented and maintained.

9.6.3. Receipt or production, arrival or initial condition, storage conditions, dispersal, and accountability of the test matrix (*e.g.,* sediment or artificial seawater) will be documented and maintained.

9.6.4. Source, receipt, arrival condition, storage conditions, dispersal, and accountability of the test organisms (including inoculum) will be documented and maintained.

9.6.5. Actual concentrations administered at each treatment level will be verified by appropriate methodologies.

9.6.6. Any data originating at a different laboratory will be identified and the laboratory fully referenced in the final report.

9.7. The following references identify analytical methods that have historically been successful for achieving the analytical quality criteria.

9.7.1. Continental Shelf Associates Report 1998. Joint EPA/Industry Screening Survey to Assess the Deposition of Drill Cuttings and Associated Synthetic Based Mud on the Seabed of the Louisiana Continental Shelf, Gulf of Mexico. Analysis by Charlie Henry Report Number IES/RCAT97–36 GC–FID and GC/MS.

9.7.2. EPA Method 3550 for extraction with EPA Method 8015 for GC–FID. EPA Method 3550C, Revision 3. February 2007. Ultrasonic Extraction. EPA Method 8015C, Revision 3. February 2007. Nonhalogenated Organics by Gas Chromatography.

9.7.3. Chandler, J.E., S.P. Rabke, and A.J.J. Leuterman. 1999. Predicting the Potential Impact of Synthetic-Based Muds With the Use of Biodegradation Studies. Society of Petroleum Engineers SPE 52742.

9.7.4. Chandler, J.E., B. Lee, S.P. Rabke, J.M. Geliff, R. Stauffer, and J. Hein. 2000. Modification of a Standardized Anaerobic Biodegradation Test to Discriminate Performance of Various Non-Aqueous Base Fluids. Society of Petroleum Engineers SPE 61203.

9.7.5. Munro, P.D., B Croce, C.F. Moffet, N.A Brown, A.D. McIntosh, S.J. Hird, and R.M. Stagg. 1998. Solid-Phase Test for Comparison for Degradation Rates of Synthetic Mud Base Fluids Used in the Off-shore Drilling Industry. *Environ. Toxicol. Chem.* 17:1951–1959.

9.7.6. Webster, L., P.R. Mackie, S.J. Hird, P.D. Munro, N.A. Brown, and C.F. Moffat. 1997. Development of Analytical Methods for the Determination of Synthetic Mud Base Fluids in Marine Sediments. *The Analyst* 122:1485–1490.

9.8 The following standards are approved for incorporation by reference by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460 and at 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: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html*.

9.8.1 ASTM International. Available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428–2959, or online at *http://www.astm.org*.

9.8.1.1 ASTM D5291–96, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants, approved April 10, 1996.

9.8.1.2 ASTM D2974–07a, Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils, approved March 15, 2007.

■ 26. Amend Appendix 5 to Subpart A of Part 435 by:

■ a. Revising the appendix heading.

■ b. Removing ''35 to 500 amu'' and adding in its place ''35 to 600 amu'' in Section 6.3.2.

■ c. Revising section 9.5. introductory text.

■ d. Revising the equation in section 9.5.2.

■ e. Revising sections 9.6, 11.3 introductory text, 11.3.1, and 11.5.4.2.

■ f. Adding section 6.17.

Appendix 5 to Subpart A of Part 435—Determination of Crude Oil Contamination in Non-Aqueous Drilling Fluids by Gas Chromatography/Mass Spectrometry (GC/MS) (EPA Method 1655)

* * * * *

9.5 Duplicates—A duplicate field sample shall be prepared and analyzed according to Section 11. The relative percent difference (RPD) of the calculated concentrations shall be less than 15%.

* * * * *

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} \times 100$$

9.6 A clean NAF sample shall be prepared and analyzed according to Section 11. Ultimately the oil-equivalent concentration from the TIC or EIP signal measured in the clean NAF sample shall be subtracted from the corresponding authentic field samples in order to calculate the true contaminant concentration (% oil) in the field samples (*see* Section 12).

* * * * *

11.3 Qualitative Identification—See Section 17 of this method for schematic flowchart.

11.3.1 Qualitative identification shall be accomplished by comparison of the TIC and EIP area data from an authentic sample to the TIC and EIP area data from the calibration standards (*see* Section 10.4). Crude oil shall be identified by the presence of C_{10} to C_{13} n-alkanes and corresponding target aromatics.

* * * * *

11.5.4.2 Asphaltene crude oils with API gravity <20 may not produce chromatographic peaks strong enough to show contamination at levels of the calibration. Extracted ion peaks should be easier to see than increased intensities for the C8 to C13 peaks. If a sample of asphaltene crude from the formation is available, a calibration standard shall be prepared.

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6.17 Schematic Flowchart for Qualitative Identification

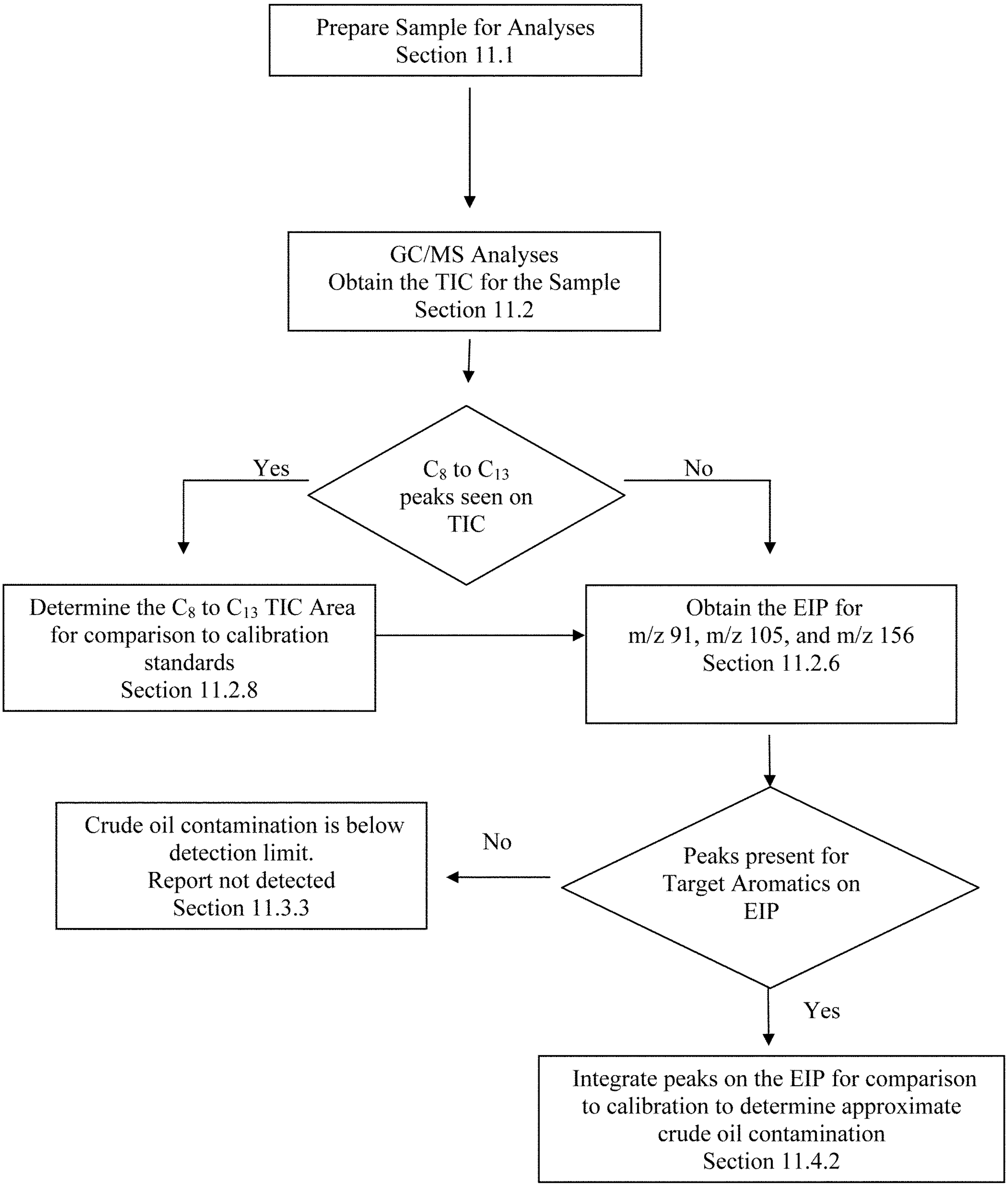

Figure 1. Schematic Flowchart for Qualitative Identification

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■ 27. The heading of Appendix 6 to Subpart A of Part 435 is revised to read as follows:

Appendix 6 to Subpart A of Part 435—Reverse Phase Extraction (RPE) Method for Detection of Oil Contamination in Non-Aqueous Drilling Fluids (NAF) (GC/MS) (EPA Method 1670)

* * * * *

■ 28. The heading of Appendix 7 to Subpart A of Part 435 is revised to read as follows:

Appendix 7 to Subpart A of Part 435—Determination of the Amount of Non-Aqueous Drilling Fluid (NAF) Base Fluid From Drill Cuttings by a Retort Chamber (Derived From API Recommended Practice 13B–2) (EPA Method 1674)

* * * * *

■ 29. Appendix 8 to Subpart A of Part 435 is amended by:

■ a. Revising the second paragraph.

■ b. Adding ''>'' before ''11–14'' in Table 1.

Appendix 8 to Subpart A of Part 435—Reference C_{16}-C_{18} Internal Olefin Drilling Fluid Formulation

* * * * *

Drilling fluid sediment toxicity ratio = 4-day LC_{50} of C_{16}-C_{18} internal olefin drilling fluid/4-day LC_{50} of drilling fluid removed from drill cuttings at the solids control equipment as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu).

* * * * *

Subpart D—Coastal Subcategory

■ 30. Section 435.41 is amended:

■ a. By revising paragraph (d).

■ b. By revising paragraph (e).

■ c. By revising paragraph (k).

■ d. By revising paragraph (m)(2).

■ e. By revising paragraph (q).

■ f. By revising paragraph (r).

■ g. By amending paragraph (w) to remove ''LC_5'' and add in its place ''LC_{50}''.

■ h. By revising paragraph (y).

■ i. By revising paragraph (ee).

■ j. By revising paragraph (ff).

■ k. By adding paragraph (mm).

§ 435.41 Special definitions.

* * * * *

(d) *Base fluid retained on cuttings* as applied to BAT effluent limitations and NSPS refers to the ''Determination of the Amount of Non-Aqueous Drilling Fluid (NAF) Base Fluid from Drill Cuttings by a Retort Chamber (Derived from API Recommended Practice 13B–2)'', EPA Method 1674, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section.

(e) *Biodegradation rate* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to the ''Protocol for the Determination of Degradation of Non Aqueous Base Fluids in a Marine Closed Bottle Biodegradation Test System: Modified ISO 11734:1995,'' EPA Method 1647, supplemented with ''Procedure for Mixing Base Fluids With Sediments,'' EPA Method 1646. Both EPA Method 1646 and 1647 are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section.

* * * * *

(k) *Diesel oil* refers to the grade of distillate fuel oil, as specified in the American Society for Testing and Materials Standard Specification for Diesel Fuel Oils D975–91, that is typically used as the continuous phase in conventional oil-based drilling fluids. This incorporation by reference was approved by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be obtained from the American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Copies may be inspected 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: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html*. A copy may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460.

* * * * *

(m) * * *

(2) *Dry drill cuttings* means the residue remaining in the retort vessel after completing the retort procedure specified in EPA Method 1674, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section.

* * * * *

(q) *Formation oil* means the oil from a producing formation which is detected in the drilling fluid, as determined by the GC/MS compliance assurance method, EPA Method 1655, when the drilling fluid is analyzed before being shipped offshore, and as determined by the RPE method, EPA Method 1670, when the drilling fluid is analyzed at the offshore point of discharge. The GC/MS compliance assurance method and the RPE method approved for use with this part are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section. Detection of formation oil by the RPE method may be confirmed by the GC/MS compliance assurance method, and the results of the GC/MS compliance assurance method shall supersede those of the RPE method.

(r) *Garbage* means all kinds of victual, domestic, and operational waste, excluding fresh fish and parts thereof, generated during the normal operation of coastal oil and gas facility and liable to be disposed of continuously or periodically, except dishwater, graywater, and those substances that are defined or listed in other Annexes to MARPOL 73/78. A copy of MARPOL may be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460.

* * * * *

(y) *No discharge of free oil* means that waste streams may not be discharged that contain free oil as evidenced by the monitoring method specified for that particular stream, *e.g.,* deck drainage or miscellaneous discharges cannot be discharged when they would cause a film or sheen upon or discoloration of the surface of the receiving water; drilling fluids or cuttings may not be discharged when they fail EPA Method 1617 (Static Sheen Test), which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section.

* * * * *

(ee) *SPP toxicity* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to the bioassay test procedure, ''Suspended Particulate Phase (SPP) Toxicity Test,'' presented in EPA Method 1619, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section.

(ff) *Static sheen test* means the standard test procedure that has been developed for this industrial subcategory for the purpose of demonstrating compliance with the requirement of no discharge of free oil. The methodology for performing the static sheen test is presented in EPA Method 1617, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section.

* * * * *

(mm) *Analytic Methods for the Oil and Gas Extraction Point Source Category* is the EPA document, EPA–821–R–11–004, that compiles analytic methods for this category. Copies may be inspected 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: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html*. A copy may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460. This method may be obtained at *http://water.epa.gov/scitech/methods/cwa/index.cfm*.

■ 31. In § 435.42 footnote 1 to the table is revised to read as follows:

§ 435.42 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

* * * * *

[1] No discharge of free oil. See § 435.41(y).

* * * * *

■ 32. In § 435.43:

■ a. Remove ''LC_5'' and add in its place ''LC_{50}'' in the table.

■ b. Footnotes 2 and 4 to the table are revised to read as follows:

§ 435.43 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable (BAT).

* * * * *

[2] As determined by the static sheen test. See § 435.41(ff).

* * * * *

[4] As determined by the suspended particulate phase (SPP) toxicity test. See § 435.41(ee).

* * * * *

■ 33. In § 435.44 footnote 2 to the table is revised to read as follows:

§ 435.44 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best conventional pollutant control technology (BCT).

* * * * *

[2] As determined by the static sheen test. See § 435.41(ff).

* * * * *

■ 34. In § 435.45:

■ a. Remove ''LC_5'' and add in its place ''LC_{50}''in the table.

■ b. Footnotes 2 and 4 to the table are revised to read as follows:

§ 435.45 Standards of performance for new sources (NSPS).

* * * * *

[2] As determined by the static sheen test. See § 435.41(ff).

* * * * *

[4] As determined by the suspended particulate phase (SPP) toxicity test. See § 435.41(ee).

* * * * *

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