

## Summary of the 2012 Method Update Rule

By

Jerry Parr

Catalyst Information Resources

[www.catalystinforesources.com](http://www.catalystinforesources.com)

EPA has published a pre-publication notice of a final rule that approves new methods, or changes to existing methods, that affect 16 EPA methods, 26 Standard Methods, 7 ASTM methods, and 8 alternate test procedures in 40 CFR Part 136. The rule also contains a number of clarifications relating to approved methods, sample preservation and holding times, and method modifications. Among the more significant changes is a new section 136.7 that would require “essential” quality control activities for all analyses. The rule will go into effect 30 days after publication in the Federal Register.

[http://water.epa.gov/scitech/methods/cwa/update\\_index.cfm](http://water.epa.gov/scitech/methods/cwa/update_index.cfm).

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

EPA approved a new version of Method 1664, *1664B: N-Hexane Extractable Material and Silica Gel Treated N-Hexane Extractable Material*. 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 A not be withdrawn immediately because many permits currently specify the use of this method.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 in the future.

EPA approved Method 200.5, *Determination of Trace Elements in Drinking Water by Axially Viewed Inductively Coupled Plasma – Atomic Emission Spectrometry*, which employs a plasma torch viewed in the axial orientation to measure chemical elements (metals). The rule also clarifies that the axial orientation of the torch is allowed for use with Method 200.7 and published Revision 4.4 of Method 200.7. Method 200.7 Revision 4.4 has also been approved for the measurement of titanium. EPA removed Method 200.7 from Table IB for the measurement of mercury. Although this pollutant is on the list of analytes in Method 200.7, mercury may be lost to the atmosphere through the use of the approved total recoverable metals digestion procedures (e.g., Method 200.2, or the digestion procedures listed in Method 200.7) that must be applied to the wastewater samples. Such losses can lead to poor recovery in the samples compared to the sample preparation procedures included in other mercury methods.

EPA approved:

- Method 525.2, an updated version of Method 525.1, as an additional approved method for all parameters for which EPA has previously approved Method 525.1.
- Pesticide Active Ingredients methods in Table IG. These methods are:
  - Method 608.1 for Organochloride Pesticides.
  - Method 608.2 for Organochlorine Pesticides.
  - Method 614 for Organophosphorus Pesticides.
  - Method 614.1 for Organophosphorus Pesticides
  - Method 617 for Organohalide Pesticides and PCBs.
  - Method 619 for Triazine Pesticides.
  - Method 622 for Organophosphorus Pesticides
  - Method 622.1 for Thiophosphate Pesticides.
  - Method 632 for Carbamate and Urea Pesticides
- Method 1627, *Kinetic Test Method for the Prediction of Mine Drainage Quality*.

EPA approved updates to Method 1622, *Cryptosporidium in Water by Filtration/IMS/FA* and Method 1623, *Cryptosporidium and Giardia in Water by Filtration/IMS/FA* to reflect changes made in the December 2005 versions of these methods. EPA approved revised versions of Methods 1103.1, 1106.1, 1600, 1603, and 1680 to correct technical errors.

EPA approved Method 624, *Purgeables*, for definitive measurements of acrolein and acrylonitrile in wastewater. EPA revised footnote 4 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.

EPA did not add Methods 1614A and Method 1668C as proposed.

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

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

EPA has changed how approved methods that are published by Standard Methods are identified. EPA now approves only the most recent version of a method published by Standard Methods by listing only one version of the method with the year of publication designated by the last four digits in the method number (e.g., Standard Method 2320 B-1997).

The following new methods or new versions were approved:

5520 B-2001 and 5520 F-2001	Oil and Grease
4500-NH3 G-1997	Ammonia (as N) and TKN
SM 4500-B B-2000	Boron
SM 4140-1997, Inorganic Ions	(Bromide, Chloride, Fluoride, Orthophosphate, and Sulfate)
3114 B-2009	Arsenic and Selenium
3114 C-2009	Arsenic and Selenium
3111 E-1999	Aluminum and Beryllium
SM 3500-Cr B-2009	Chromium
SM 4500-Norg D-1997	Kjeldahl Nitrogen
SM 3112 B-2009	Mercury
SM 4500-P G-1999 and SM 4500-P H-1999	Phosphorus, Total
SM 4500-P E-1999 and SM 4500-P F-1999	Phosphorus, Total
SM 4500-O B, D, E and F-2001	Oxygen, Dissolved
SM 4500-O D-2001	Oxygen, Dissolved
SM 4500-O E-2001	Oxygen, Dissolved
SM 5530 B-2005	Phenols
SM 5530 D-2005	Phenols
SM 3500-K C-1997	Potassium, Total
SM 2540 E-1997	Residues – Volatile
SM 4500-SiO2 E-1997 and SM 4500-SiO2 F-1997	Silica, Dissolved
SM 4500-SO4 <sup>2-</sup> C-1997, D-1997, E-1997, F-1997 and G-1997	Sulfate,

2-	SM 4500-S B-2000 and C-2000	Sulfide
----	-----------------------------	---------

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.

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

EPA approved 4 new or revised ASTM methods for cyanide:

- D2036-09 Standard Test Methods for Cyanides in Water.
- D6888-09 Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection.
- D7284-08 Standard Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection.
- D75 11 -09e2 Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection.

Because there were no EPA-approved methods for free cyanide when water quality criteria were established for free cyanide EPA recommended measurement of cyanide after a “total” distillation. Analytical methods for free cyanide have been developed, and EPA added free cyanide as a parameter (24A in Table IB.) D4282-02 determines free cyanide as the cyanide that diffuses into a sodium hydroxide solution from a solution at pH 6. It is not applicable to cyanide complexes that resist dissociation, such as hexacyanoferrates and gold cyanide, and it does not include thiocyanate and cyanohydrin.

Other approved methods proposed:

- D888-09 Standard Test Method for Dissolved Oxygen in Water. This method may be used for BOD and Carbonaceous Oxygen Demand CBOD.
- D7573-09 Standard Test Method for Total Carbon and Organic Carbon in Water by High Temperature Catalytic Combustion and Infrared Detection.
- D7065-06: Standard Test Method for Determination of five chemicals: Nonylphenol (NP), Bisphenol A (BPA), p-tert-Octylphenol (OP), Nonylphenol Monoethoxylate (NP1EO), and Nonylphenol Diethoxylate (NP2EO) in Environmental Waters by Gas Chromatography Mass Spectrometry.

EPA did not add ASTM Methods D7574-09 and D7485-09 as proposed.

### D. Changes to Alternate Test Procedures

EPA approved eight alternate test procedures. These new methods are:

- Hach Company’s Method 10360 Luminescence Measurement of Dissolved Oxygen (LDO®) in Water,
- In-Situ Incorporated’s
  - Method 1002-8-2009 Dissolved Oxygen (DO) Measurement by Optical Probe,
  - Method 1003-8- 2009 Biochemical Oxygen Demand (BOD) Measurement by Optical Probe, and
  - Method 1004-8- 2009 Carbonaceous Biochemical Oxygen Demand (CBOD) Measurement by Optical Probe August 2009,
- Mitchell Method M5271 and M5331 for measuring turbidity in wastewater;

- Thermo Scientific's Orion Method AQ4500 for measuring turbidity in wastewater; and
- Systema Scientific, LLC's Easy (1-Reagent) Nitrate Method.

## **E. Clarifications and Corrections to Previously Approved Methods**

EPA clarified the purpose of the immediate filtration requirement in orthophosphate measurements, which 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). This filtration excludes any particulate forms of phosphorus that might hydrolyze into orthophosphorus in a slightly acidic sample during the allowed 48 hour holding time. Each grab sample must be filtered within 15 minutes of collection to prevent orthophosphate formation. Specifically, filtration may not be delayed until the final grab sample is collected; each grab sample must be filtered upon collection. However, the filtered grab samples may be held for compositing up to the 48-hour holding time. EPA added a footnote (24) to Table II providing this clarification.

EPA corrected missing citations to the table of microbiological methods for ambient water monitoring which are specified in Table IH. Stakeholders asked EPA to separately specify the microbiological methods that EPA has approved for wastewater (Table IA) from those for ambient water. In the final rule of March 26, 2007, EPA inadvertently omitted fecal coliform, total coliform, and fecal streptococcus methods from the table. This omission is corrected in today's rule.

EPA added language to the end of footnote 63 to clarify that the Hach Method 10360 for measurement of dissolved oxygen can be used in conjunction with the methods approved for measurement of biochemical demand (BOD) and carbonaceous biochemical oxygen demand (CBOD).

EPA also corrected a number of typographical errors in the tables and footnotes, correcting spelling and method availability information, method title names, and document identification numbers.

## **F. Proposed Revisions to Required Containers, Preservation Techniques, and Holding Times**

EPA revised footnote 22 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." EPA also revised footnote 4 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.

The cyanide sample handling instructions in Footnote 5 of Table II were revised to recommend the treatment options for samples containing oxidants described in ASTM's sample handling practice for cyanide samples, D7365-09a. This practice advises analysts to add a reducing agent only if an oxidant is present, and use of the reducing agents sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), ascorbic acid, sodium arsenite (NaAsO<sub>2</sub>), or sodium borohydride (NaBH<sub>4</sub>).

The cyanide sample handling instructions in Footnote 6 of Table II were revised to describe options available when the interference mitigation instructions in D7365-09a are not effective, allowing 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.

Footnote 16 for handling Whole Effluent Toxicity (WET) samples was revised by adding two sentences. The two sentences are "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.” In addition, EPA will post, on the WET website, corrections to errata in the “Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms” manual.

Footnote 4 was revised to clarify the sample holding time for the Whole Effluent Toxicity (WET) samples for the three toxicity methods to indicate that one sample of the minimum of three required samples may be used for the renewal of the test solutions and that the sample holding time refers to first use of each sample collected for the toxicity test.

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 Methods 1650 and 1653 from Part 430 to Table IC, EPA inadvertently omitted the associated parameters to Table II, and is correcting this omission.

### **G. Revisions to 136.4 and 136.5 for Alternate Test Procedures**

The procedures for obtaining review and approval for the use of alternate test procedures (alternate methods or ATPs) have been clarified. Separate sections describe the procedures for obtaining EPA review and approval for nationwide use, and the procedures for obtaining approval for limited use.

Today’s rule finalizes these sections as proposed with one exception. EPA received comments that the proposed language 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.

### **H. Revisions to Method Modification Provisions**

EPA encourages regulatory authorities to allow analysts the flexibility to modify CWA methods without prior approval provided the user has documented equivalent or better performance of the method in the matrix type to which the user will apply the modified method. EPA recognizes that addressing specific matrix interferences may require modifications to approved methods that do not require the extensive review and approval process specified for an alternate test procedure. Based on users’ experiences with 136.6, since it was promulgated on March 12, 2007, EPA revised this section 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 employed in methods currently approved in Part 136. Analysts may use the examples in this section to assess and document that their modification is acceptable and does not depart substantially from the chemical principles in the method being modified.

The additional examples provide further guidance to laboratories and permittees on allowable method modifications that do not require an application through the ATP program. Today’s rule includes the following revisions to the regulatory text: (a) adds language to clarify that modifications to sample collection, preservation, and holding time do not fall within the scope of 136.6, (b) revises the language to 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) 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.

### **I. New Quality Assurance and Quality Control Language**

EPA has specified “essential” quality control at Part 136.7 for use in conducting an analysis with an approved method and when insufficient instructions are contained in an approved method. Auditors, co-regulators, laboratory personnel, and the regulated community have noted the different amounts and types of quality assurance (QA) and quality control (QC) procedures practiced by laboratories that use Part 136 methods. Some of these methods are published by voluntary consensus standards bodies, such as Standard Methods, and ASTM. Each organization has its unique 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 elsewhere. For example, in Standard Methods each specific Part and section can contain additional QA and QC requirements. ASTM specifies QA and QC requirements in the Referenced Documents section and in the analyte method. Both organizations require the analyst to reference this additional information to achieve the QA and QC expected for valid results.

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 specific method, or referenced these procedures by other means. Consequently, today’s rule clarifies that an analyst using these methods will also comply with the QA/QC requirements listed in the appropriate sections. 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 Part 136 for analysis of pollutants. For methods that have insufficient QA/QC requirements, analysts could refer to and follow the QC published in several public sources. In addition to and regardless of the source of the laboratory’s QA and QC instructions, EPA specified twelve essential quality control checks that must be in the laboratory’s documented quality system unless a written rationale is provided to explain why these controls are inappropriate for a specific analytical method or application. This written rationale will be included in the laboratory’s Standard Operating Procedure (SOP) for each method to which specific controls do not apply (e.g., internal standards, surrogate standards or tracers do not apply to analyses of inorganic parameters) as well as being included with the monitoring data produced using each method. 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.

### **J. Withdrawal of Appendices at 40 CFR 136**

EPA proposed to incorporate by reference in Table IB all of the methods printed in 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 Method 200.7. However, Federal regulations at 1 CFR Part 51.7 prohibit the incorporation by reference of material previously published in the Federal Register. Thus, EPA is not withdrawing Appendices A or C. Because 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.

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 Method 279.2 for thallium and Method 289.2 for zinc, and corrects typographical errors in the Appendix.

#### **K. Revisions to Part 423 for Steam Electric Power Generators**

EPA revised the definitions for *total residual chlorine* and *free available chlorine*. The current definitions restrict the permittee to the use of the specific amperometric titration method cited in the definitions. The revised definitions will allow the permittee flexibility to use additional approved methods.

- 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 136.3(a), or other methods approved by the permitting authority.
- The term *free available chlorine* means the value obtained using any of the “chlorine – free available” methods in Table IB 136.3(a) where the method has the capability of measuring free available chlorine, or other methods approved by the permitting authority.

#### **L. Revisions at 40 CFR 430 (Pulp, Paper, and Paperboard Point Source Category)**

EPA also proposed to remove Appendix A at Part 430 and to incorporate by reference the methods in this Appendix. Appendix A contains two methods, Method 1650 for adsorbable organic halides or AOX, and Method 1653 for chlorinated phenolics. As explained above, EPA cannot incorporate by reference this material, so Appendix A remains unchanged. EPA added these two methods to Table IC for general use.

#### **M. Revisions at 40 CFR 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 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. This approach organizes the analytical methods for the Offshore Subcategory into one document and allows for easier access to the methods for this category.

EPA is also incorporating additional quality assurance procedures in the marine anaerobic biodegradation method (Appendix 4) and is correcting some erroneous references and omissions in the method for identification of crude oil contamination (Appendix 5) into the new document (EPA821-R-11-004).

Additionally, as proposed, EPA corrected some erroneous references and omissions in the method for identification of crude oil contamination (Appendix 5), as follows:

- Adding a schematic flow for qualitative identification of crude oil,
- Correcting erroneous citations in sections 9.5, 9.6, 11.3, and 11.3.1 of Appendix 5, and
- Adding a missing “<” (less than) sign for identification of crude oil contamination in the asphaltene crude discussion at Section 11.5.4.2.