

EPA Finalizes “Method Update Rule” for Water Program

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On April 18, 2012, EPA published a pre-publication notice of a final rule that approves new methods, or changes to existing methods, that affects over 100 EPA methods, Standard Methods, ASTM methods, and other 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, expected in late May or early June. http://water.epa.gov/scitech/methods/cwa/update_index.cfm.

Note: The preamble to this final rule did not mention all the changes that appeared in the final rule. Catalyst has performed a detailed side-by-side comparison of the current promulgated version of Part 136 to the final rule published in April and has prepared a redline version of Part 136 available on the Catalyst website at www.catalystinforesources.com. In this summary, changes made to the rule that were not discussed by EPA are noted.

A. 136.3 Test Procedures

Section 136.3 lists all analytes in the water program along with approved methods. Tables 1A, 1B, 1C, 1D and 1H were all significantly revised with new and updated methods, new analytes, and new and revised footnotes to the tables. The references section was also completely revised. Note that 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).

A.1 Tables 1A and 1H: Approved Methods for Microbiological Analytes

In the 2007 method update rule, EPA split Table 1A into two tables, one for wastewater analyses and one for ambient water. In this rule, EPA has approved some updated methods and corrected errors from the 2007 rule.

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 inadvertently omitted fecal coliform, total coliform, and fecal streptococcus methods from table 1H. This omission was corrected

Table 1B: Approved Methods for Inorganic Analytes

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.

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. 200.7 is approved for the analysis of 28 metals while 200.5 is approved for only 23 metals.

EPA removed all ICP methods from Table IB for the measurement of mercury. Although this pollutant is on the list of analytes in several approved methods, mercury may be lost to the atmosphere through the use of the approved total recoverable metals digestion procedures 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 also approved Method 1627, *Kinetic Test Method for the Prediction of Mine Drainage Quality*, and added Acid Mine Drainage as an analyte to Table 1B.

The following new Standard Methods or new versions were approved:

5520 B- and F-2001	Oil and Grease
4500-NH ₃ G-1997	Ammonia (as N) and TKN
4500-B B-2000	Boron
4140-1997	Bromide, Chloride, Fluoride, Orthophosphate, and Sulfate
4110 C- and D-2000*	Bromide, Chloride, Fluoride, Orthophosphate, and Sulfate
3114 B-2009	Arsenic and Selenium
3114 C-2009	Arsenic and Selenium
3111 E-1999	Aluminum and Beryllium
3525 B-2009*	ICP/MS for 26 metals
4500-Cl D-, E-, F, and G- 2000*	Free Available Chlorine
3500-Cr B-2009	Chromium
4500-Norg D-1997	Kjeldahl Nitrogen
3112 B-2009	Mercury
4500-P G- and P H-1999	Phosphorus, Total
4500-P E- and P F-1999	Phosphorus, Total
4500-O B, D, E and F-2001	Oxygen, Dissolved
4500-O D-2001	Oxygen, Dissolved
4500-O E-2001	Oxygen, Dissolved
5530 B-2005	Phenols
5530 D-2005	Phenols
3500-K C-1997	Potassium, Total
2540 E-1997	Residues – Volatile
4500-SiO ₂ E- and F-1997	Silica, Dissolved
4500-SO ₄ ²⁻ C-, D-, E-, F- and G-1997	Sulfate
4500-S ²⁻ B- and C-2000	Sulfide

* This method is not mentioned in the preamble to the final rule.

Note that free available chlorine (defined in Part 423 as “the value obtained using any of the chlorine – free available methods in Table IB”) was added as a new analyte to Table 1B and 4 Standard Methods were approved for this analyte.

EPA added SM 3113B-2004 for the measurement of cadmium, chromium, iron, lead, and silver, because EPA stated these analytes are covered by the method and exhibit acceptable analytical performance. EPA also added SM 3113B-2004 for the measurement of gold and cadmium, but this addition was not discussed in the preamble.

EPA approved 4 new or revised ASTM methods for total cyanide:

- D2036-09
- D6888-09
- D7284-08.
- D7511-09

EPA added free cyanide as a new analyte in Table IB and approved ASTM methods D4282-02 and D7237-10* for this new analyte.

Other approved new ASTM methods:

- D888-09 Dissolved Oxygen.
- D7573-09 Total Carbon and Organic Carbon
- D1976-07 Metals by ICP/AES*
- D1253-08 Free Available Chlorine*
- D6508-00 (05) Anions*
- D1426-08 TKN*
- D1783-01 Phenols*
- D5697-03 Residue (Total and filterable)*

*This method not mentioned in the preamble.

EPA approved D5673-05 for additional metals (Au, Mg, K, Si, Na, Sn, and Ti); this approval was not discussed in the preamble. EPA also updated 29 ASTM methods to more recent editions. These updated methods were not discussed in the preamble.

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

- Hach Company’s Method 10360 Luminescence Measurement of Dissolved Oxygen (LDO),
- In-Situ Incorporated’s
 - Method 1002-8-2009 for Dissolved Oxygen,
 - Method 1003-8- 2009 for Biochemical Oxygen Demand (BOD), and
 - Method 1004-8- 2009 for Carbonaceous Biochemical Oxygen Demand (CBOD),
- Mitchell Method M5271 and M5331 for turbidity;
- Thermo Scientific’s Orion Method AQ4500 for turbidity; and
- Systea Scientific, LLC’s Easy (1-Reagent) Nitrate Method for nitrate and nitrate-nitrite.

EPA also approved 2 USGS methods for metals (I-2057-90 and I-4020-05) and approved an AOAC method (993.14) for an additional four metals. These three methods were also not mentioned in the preamble.

EPA also revised several footnotes to Table 1B and added 12 footnotes. Most of the new footnotes are citations on where to find the newly approved methods, but the following are significant changes:

- Footnote 5 allows for catalysts other than copper sulfate for TKN*,
- Footnote 6 has an additional discussion on the distillation step for NH₃*,
- Footnote 30 (previously 60) allows for the use of alternate complexing reagent for Method 350.1 for ammonia*,
- Footnote 38 specifies purity of n-Hexane for Method 1664*,
- Footnote 60 has a caution for Method 4500-NH₃ F*,
- Footnote 61 allows for the use of the colorimetric method for Be (3500-Be D), but discouraged*, and
- Footnote 63 indicates the Hach LDO method can be used for BOD and COD.

* This footnote not discussed in the preamble.

Table 1C: Approved Methods for Organic Analytes

EPA approved Method 624 for the 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 approved D7065-06 for the determination of nonyl phenols and added 5 analytes to Table 1C: Nonylphenol (NP), Bisphenol A (BPA), p-tert-Octylphenol (OP), Nonylphenol Monoethoxylate (NP1EO), and Nonylphenol Diethoxylate (NP2EO).

EPA added two methods, Method 1650 for adsorbable organic halides or AOX, and Method 1653 for chlorinated phenolics. These two methods are used for the pulp and paper industry and have been approved in Part 430 for many years. AOX and chlorinated phenolics were also added to Table 1C as new analytes. The analyte “chlorinated phenolics” is actually 12 specific compounds listed in Part 423.

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

Table 1C: Approved Methods for Pesticides

EPA approved 19 EPA methods, 3 Standard Methods*, 2 ASTM methods* and 6 USGS methods* for pesticides in Table ID. The EPA methods approved are:

- 505*
- 507*
- 508*
- 525.1
- 525.2
- 531.1*
- 553*
- 608.1
- 608.2
- 614
- 614.1
- 615
- 617
- 619
- 622
- 622.1
- 632
- 1656*
- 1657*

*These methods not mentioned in the preamble.

With the addition of these new methods, Thin Layer Chromatography methods published in 1978 for 16 pesticides, while still allowed, are not the only methods for these pesticides. This rule change does allow for many more method options for the “priority pollutant” pesticides.

Table 1G: Approved Methods for Pesticide Active Ingredients

Method 525.2, an updated version of Method 525.1, was approved as an additional approved method for pesticide active ingredients. EPA also deleted Method 525.1 as an approved method for the measurement of ametryn, diazinon, disulfoton, prometon, and trifluralin.

Table II: Required Containers, Preservation Techniques, and Holding Times

E. coli and enterococcus EPA changed the holding time to 8 hours and 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.

Cyanide The cyanide sample handling instructions in Footnote 5 were revised to recommend the treatment options for samples containing oxidants described in ASTM’s sample handling practice for cyanide samples, D7365-09. This practice advises analysts to add a reducing agent only if an oxidant is present, and use of the reducing agents sodium thiosulfate (Na₂S₂O₃), ascorbic acid, sodium arsenite (NaAsO₂), or sodium borohydride (NaBH₄). The cyanide sample handling instructions in Footnote 6 were revised to describe options available when the interference mitigation instructions in D7365-09 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. The pH for preservation for cyanide was changed from > 12 to >10, but this may be an error.

Orthophosphate 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 footnote 24 providing this clarification.

Whole Effluent Toxicity 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 announced it 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 that were added to Table 1C. Free cyanide was also added

Cryptosporidium and Giardia The preservation temperature was changed from 0 — 8 to <1 — 10 degrees C. This change was not discussed in the preamble.

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. Section 136.4 describes the procedures for obtaining EPA review and approval for nationwide use, and Section 136.5 describes the procedures for obtaining approval for limited use.

136.6 Revisions to Method Modification Provisions

EPA revised this section to provide many 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 without approval from EPA. 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.

Examples of Allowed Modifications

- Changes between manual method, flow analyzer and discrete instrumentation.
- Changes between automated and manual sample preparation.
- Use of interference reduction for ICP-MS.
- Using a different acid to adjust pH in colorimetric methods.
- Changes in calibration model.
- Use of Relative Standard Error (RSE).
- Use of prepackaged reagents.
- Use of Selected Ion Monitoring (SIM).
- Changes in purge-and-trap sample volumes or operating conditions.
- Combine base/neutral and acid fractions for Method 625.

136.7 New Quality Assurance and Quality Control Language

EPA has specified twelve “essential” quality control requirements that must be performed when conducting an analysis with an approved method or when insufficient instructions are contained in an approved method unless a written rationale is provided to explain why these controls are inappropriate for a specific analytical method or application.. 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. For methods that have

insufficient QA/QC requirements, analysts could refer to and follow the QC published in several sources. 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:

- (1) Demonstration of Capability (DOC);
- (2) Method Detection Limit (MDL);
- (3) Laboratory reagent blank (LRB), also referred to as method blank (MB);
- (4) Laboratory fortified blank (LFB), also referred to as a spiked blank, or laboratory control sample (LCS);
- (5) 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;
- (6) Internal standards (for GC/MS analyses), surrogate standards (for organic analysis) or tracers (for radiochemistry);
- (7) Calibration (initial and continuing), also referred to as initial calibration verification (ICV) and continuing calibration verification (CCV);
- (8) Control charts (or other trend analyses of quality control results);
- (9) Corrective action (root cause analysis);
- (10) QC acceptance criteria;
- (11) Definitions of preparation and analytical batches that may drive QC frequencies; and
- (12) Minimum frequency for conducting all QC elements.

Appendix C Method 200.7

The version of method 200.7 previously published in Appendix C has been replaced with a version stated in the preamble to be Revision 4.4, 1994. Neither the date or revision number is shown in the published method, but a detailed comparison by Catalyst has verified that this is in fact Revision 4.4.

Appendix D Precision and Recovery Statements for EPA Methods for Metals

The rule also removed 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.