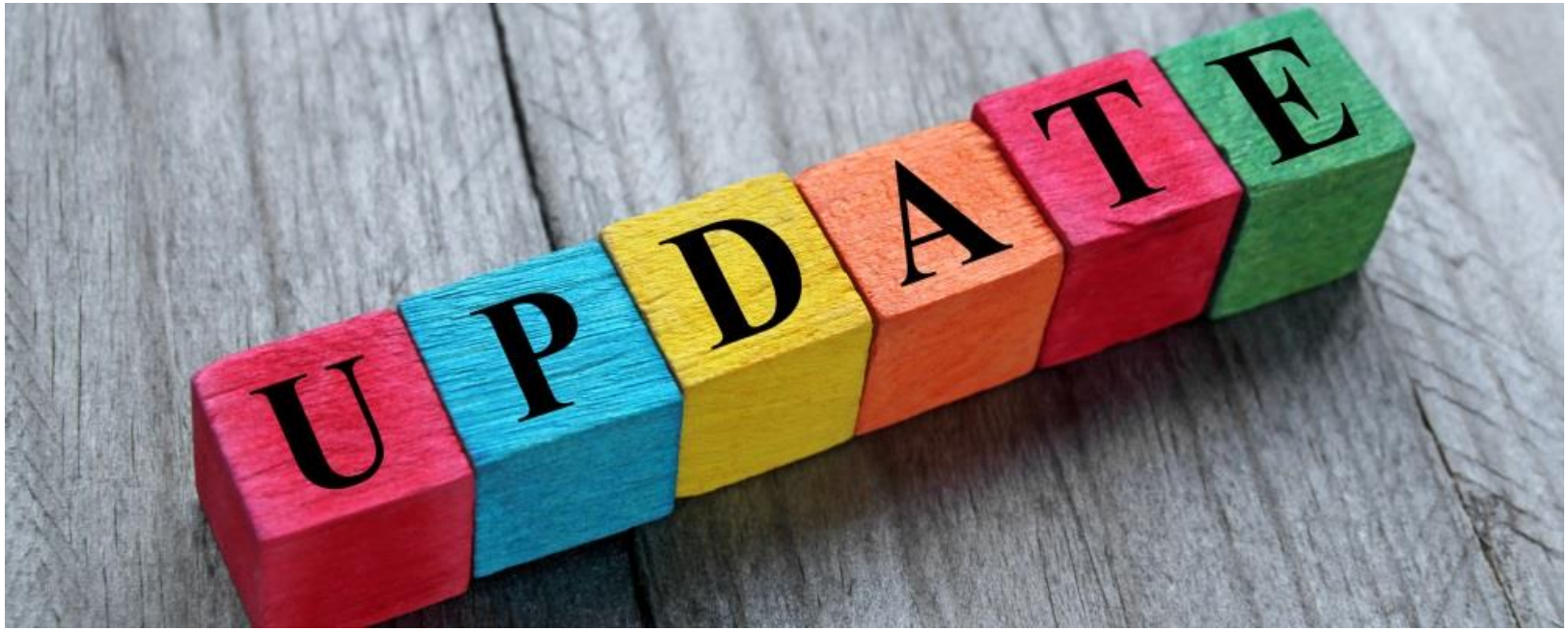
The 2021 Method Update Rule



Jerry Parr

Disclaimer

- There was a lot of information reviewed, and some errors may exist. **Read the Rule and the Methods that affect you!**

AGENDA

- New and Revised Methods
  - EPA
  - Standard Methods
  - ASTM
  - Other
- Other Changes
  - Table 1A and 1H
  - Table 1B
  - Method modifications
  - Other minor corrections
- Implementation

2021 Methods Update Rule

- Finalized May 19, 2021
- Effective July 19, 2021
- One Updated EPA Method (1623.1)
- New and Updated Standard Methods
- New and Updated ASTM methods
- New and Updated methods from other sources
- Changes to sample preservation and holding times
- Addition of microwave digestion for metals
- Other “Technical Corrections”

Redline version available on request

Changes to Part 136

- 136.3 Test Procedures
- 136.4 Regional ATP
- 136.5 National ATP
- 136.6 Method Flexibility
- 136.7 Essential QC
- Appendix A 600 Methods
- Appendix B MDL
- Appendix C 200.7
- Appendix D P/A data

Changes to Section 136.3

- Subjection (a)
  - Table 1A Biological (WW)
  - Table 1B Inorganics
  - Table 1C Non-Pesticide Organics
  - Table 1D Pesticides
  - Table 1E Radiological
  - Table 1F Pharmaceutical
  - Table 1G Pesticide Active Ingredients
  - Table 1H Biological (Ambient)
  - Table II Containers and Holding Times
- Subsection (b)
  - Updated References, Sources, and Table Citations

Tables 1 A and 1H. Bacteria

Table 1 A

- Updated methods
  - SM 9221 B, E, F, I-14
  - SM 9222 B, D-14
  - SM 9223-B-16
  - SM 9230 B, C, D-16
- New Method
  - SM 9221F-14
- Deleted Method
  - SM 9221 C-06
- Other
  - Moved Colilert 18 (Coliform, fecal) to Parameter 2
  - Deleted Parameter 4 and "in presence of chlorine"

Table 1 H

- Updated methods
  - SM 9222B-06
  - SM 9222D and G-06
  - SM 9213-07

Changes in Column 1 to ensure 9222 D and E could be used for biosolids and a statement that wastewater unlikely to contain chlorine

Changes to Footnotes in Tables 1A and 1H

- Revised 11 by changing "Approved" to "Recommended."
  - Four methods are approved for coliform in biosolids. EPA believes Methods 1680 and 1681 are preferred because "more method validation data is available."
- Deleted "~~where, for example, a substrate is used to detect the enzyme [beta]glucuronidase produced by E. coli~~" from 13.
- Added Quanti-Tray 2000 to footnotes 16 and 18
- Deleted 21: ~~Recommended for enumeration of target organism in wastewater effluent~~
- Revised 29 by changing "the medium" to "positive sample."
- Revised 30 as follows:
  - On a monthly basis, at least ten sheen colonies from ~~the medium~~ positive samples must be verified using lauryl tryptose broth and brilliant green lactose bile broth, ….

Changes to Footnotes in Tables 1A and 1H

- Added 31-33
  - Subject coliform positive samples determined by 9222 B-2015 or other membrane filter procedure to 9222 I-2015 using NA-MUG media.
  - Verification of colonies by incubation of BHI agar at 10 ± 0.5 °C for 48 ± 3 h is optional. As per the Errata to the 23rd Edition of *Standard Methods for the Examination of Water and Wastewater* "Growth on a BHI agar plate incubated at 10 ± 0.5 °C for 48 ± 3 h is further verification that the colony belongs to the genus *Enterococcus*."
  - This procedure [9221 F] allows for simultaneous detection of *E. coli* and thermotolerant coliforms by adding inverted vials to EC-MUG; the inverted vials collect gas produced by thermotolerant coliforms.

Methods 1623.1, 1680, and 1681

1623.1

- Includes updated acceptance criteria for IPR, OPR, and MS/MSD, and clarifications and revisions based on user questions and feedback about Method 1623 over the past 19 years.

1680 and 1681 (Footnote 11)

- Clarified that Methods 1680 and 1681 are "recommended" over SM 9221 E because "more method validation data is available."

One New Method for Table 1H

Method Number	**Method Name**
Micrology Laboratories, LLC. KwikCount	Rapid Detection of E. coli in Beach Water by EC Membrane Filtration

Tables 1 A. Aquatic Toxicity

Table 1 A

- Updated Descriptions for EPA WET Methods
  - Added common name of species
  - Updated footnotes 25-27 by adding 2016 Errata Sheet

WET Errata Sheet (2016)

- Now cited in Footnotes to Table 1A
  - Available at: https://www.epa.gov/cwa-methods/whole-effluent-toxicity-methods
  - <Download the Manual> to access
- Many changes
  - Some trivial such as “Add ‘test’ between ‘minimum’ and ‘acceptability criteria.’ "
  - Some significant such as “Replace the graphs in Figure 1 with log scale graphs.”

Table 1B. Updated Standard Methods

Method	Analyte(s)	Change
2540 B, C, D, E, and F-15	total, filterable, non-filterable, volatile, and settleable residue	
4500-CN- (B-F)-16	cyanide	
4500-CN- G-16	cyanide available (cyanide amenable to chlorination (CATC))	
4500-NO_3^- D-16	nitrate (as nitrogen)	
4500-NO_3^- (E, F, and H)-16	nitrate-nitrite (as nitrogen),	
4500-NO_3^- (E and F)-16	nitrite (as nitrogen)	
4500-O (B-F, and G)-16	oxygen (dissolved)	
5210 B-16	biochemical oxygen demand (BOD_5) and carbonaceous biochemical oxygen demand ($CBOD_5$)	
5310 (B, C)-14	total organic carbon (TOC)	

Table 1B. New Standard Methods

Method	Analyte(s)	Technology
4500-CN^- N-16	Cyanide, total	semi-automated spectrophotometry.
4500-NO_3^- I-16	combined nitrate-nitrite, nitrite (bypass the reduction column) and nitrate by subtraction	automated cadmium reduction and spectrophotometry
4500-NO_3^- J-18	combined nitrate-nitrite, nitrite when bypassing the enzymatic reduction step, and nitrate by subtraction	enzymatic reduction followed by colorimetric, manual
4500-O H-16	dissolved oxygen	luminescent-based sensor

TBLE 1B. Updated ASTM Methods

Inorganic Non-Metals (Except Nitrogen and Cyanide)		
Method	**Analyte**	**Comment**
D1067-16	Acidity	No procedural changes.
D1067-16	Alkalinity	No procedural changes.
D1126-17	Hardness	No procedural changes.
D1179-16 (A, B)	Fluoride	No procedural changes.
D1246-16	Bromide	No procedural changes.
D3867-16 (A, B	No_3, No_2	Added more detailed QC requirements, including laboratory control sample (LCS), method blank, and matrix spike analyses. Added specifications for filter paper. Changed the LCS frequency from 10% of samples to once per batch (up to 20) and sets the CCB and CCV frequencies at 10%.
D4327-17	Anions: Br, F, No_3, No2, Po_4, SO_4,	Updated the equipment and reagent descriptions to reflect more modern instrumentation, such as use of hydroxide eluents and eluent regeneration systems.
D4658-15	Sulfide	No procedural changes.
D512 (A, B)-12	Chloride	Corrected one term in the calculation of the chloride calculation.
D516-16	Sulfate	Added specifications for filter paper.
D5257-17	Chromium, +6	Added a few additional warnings or recommendations.
D6508-15	Anions: Br, Cl, F, No_3, Po_4, SO_4	No procedural changes.
D888-12 (A–C)	Oxygen, dissolved	Added information on a two-point calibration and updated performance information from an interlaboratory study to D888-12 (C).

TABLE 1B. Updated ASTM Methods

Nitrogen Species		
Method	**Analyte**	**Comment**
D1426-15 (A, B)	Ammonia	A lengthy section of QC requirements was added to the D1426A) that parallels the QC discussion that was already in the B procedure. Both procedures added information on use of commercially prepared standards and filter paper
D1426-15 (A, B)	Ammonia	QC requirements were added to D1426A that parallels the QC discussion that was already in the B procedure. Both procedures added information on use of commercially prepared standards and filter paper.
D3590-17 (A, B)	Nitrogen, Kjeldahl	Changed the acceptance limit for the CCV from 10% to 15% and adds a requirement for a CCB. Given that neither the approved Standard Methods method for measuring ammonia after the TKN digestion, nor the comparable EPA Method 350.1, include a CCV requirement or an acceptance limit, the change of the acceptance limit from 10% to 15% in the revised ASTM method represents a requirement that is more stringent than that required in other approved procedures and therefore is not an impediment to its approval.
D3867-16 (A, B	NO_3, NO_2	Added more detailed QC requirements, including laboratory control sample (LCS), method blank, and matrix spike analyses. Added specifications for filter paper. Changed the LCS frequency from 10% of samples to once per batch (up to 20) and sets the CCB and CCV frequencies at 10%.

TABLE 1B. Updated ASTM Methods

Cyanide Species		
Method	**Analyte**	**Comment**
D2036-09 (A, B) (15)	Cyanide, available	No procedural changes.
D2036-09 (A, B) (15)	Cyanide, total	No procedural changes.
D2972-15 (A–C)	Arsenic	QC frequencies for method blank, CCV, CCB, matrix spike, and duplicate analyses are now tied to a laboratory-defined batch of up to 20 samples.
D4282-15	Cyanide, free	No procedural changes.
D6888-16	Cyanide, available	Added a new mixed ligand exchange reagent, but also retains the original two ligand reagents that had to be mixed together during the testing.
D7237-15 (A)	Cyanide, free	Applicable range of the method has been changed from 2 to 500 µg/L to 5 to 500 µg/L. New information about interferences from floatation reagents has been added to Section 6.3. New materials in Section 8 discuss alternative reagents or concentrations.
D7284-13 (17)	Cyanide, total	No procedural changes.
D7511-12 (17)	Cyanide, total	No procedural changes.

TABLE 1B. Updated ASTM Methods

Metals Part 1		
Method	**Analyte**	**Comment**
D1068-15 (A-C)	Iron	Added specifications for filter paper.
D1687-17 (B, C)	Chromium	The QC frequencies for method blank, continuing calibration verification (CCV), continuing calibration blank (CCB), matrix spike, and duplicate analyses are now tied to a laboratory-defined batch of up to 20 samples.
D1687-17 (B, C)	Chromium, hexavalent	The QC frequencies for method blank, continuing calibration verification (CCV), continuing calibration blank (CCB), matrix spike, and duplicate analyses are now tied to a laboratory-defined batch of up to 20 samples.
D1688-17 (A–C)	Copper	Clarified the requirements for a multi-point calibration by discussing it in the calibration section as well as the QC section of all three procedures. The QC frequencies for method blank, CCV, CCB, matrix spike, and duplicate analyses are now tied to a laboratory-defined batch of up to 20 samples.
D1691-17 (A, B)	Zinc	QC frequencies for method blank, CCV, CCB, matrix spike, and duplicate analyses are now tied to a laboratory-defined batch of up to 20 samples.
D1886-14 (A–C)	Nickel	QC frequencies for method blank, CCV, CCB, matrix spike, and duplicate analyses are now tied to a laboratory-defined batch of up to 20 samples.
D2972-15 (A–C)	Arsenic	QC frequencies for method blank, CCV, CCB, matrix spike, and duplicate analyses are now tied to a laboratory-defined batch of up to 20 samples.

TABLE 1B. Updated ASTM Methods

Metals Part 2		
Method	**Analyte**	**Comment**
D3223-17	Mercury	Changed the acceptance limit for the CCV from 10% to 15% and added a requirement for a CCB. Given that the most comparable EPA procedure, Method 245.1, does not include a CCV requirement or an acceptance limit, the change of the acceptance limit from 10% to 15% in the revised method represents a requirement that is more stringent than that in EPA's procedure and therefore, the change is not an impediment.
D3373-17	Vanadium	Clarified the requirements for a multi-point calibration by discussing it in the calibration section as well as the QC section of all three procedures. The QC frequencies for method blank, CCV, CCB, matrix spike, and duplicate analyses are now tied to a laboratory-defined batch of up to 20 samples.
D3557-17 (A–D)	Cadmium	Clarified requirements for a multi-point calibration by discussing it in the calibration section as well as the QC section of all three procedures. The QC frequencies for method blank, CCV, CCB, matrix spike, and duplicate analyses are now tied to a laboratory-defined batch of up to 20 samples, as opposed to 10 samples previously.
D3558-15 (A–C)	Cobalt	Clarified requirements for a multi-point calibration by discussing it in the calibration section as well as the QC section of all three procedures. The QC frequencies for method blank, CCV, CCB, matrix spike, and duplicate analyses are now tied to a laboratory-defined batch of up to 20 samples, as opposed to 10 samples previously.

TABLE 1B. Updated ASTM Methods

Metals Part 3		
Method	**Analyte**	**Comment**
D3559-15 (A–D)	Lead	Clarified the requirements for a multi-point calibration by discussing it in the calibration section as well as the QC section of all three procedures. Also added a new section with the QC requirements to the direct AA procedure that was already present in the AA furnace portion of this procedure (D3559-15 [D]).
D3645-15 (A, B)	Beryllium	Added specifications for filter paper. Clarified the requirements for a three-point calibration by discussing it in the calibration section as well as the QC section of both procedures. Added a new section with the QC requirements to the direct aspiration AA procedure that was already present in the AA furnace portion of this procedure (D3645-15 [B]).
D3859-15 (A, B)	Selenium	The changes to the gaseous hydride portion of the method clarified the requirement for a 6-point calibration by discussing it in the calibration section as well as the QC section. Added an updated discussion of block digesters. The QC frequencies for method blank, CCV, CCB, matrix spike, and duplicate analyses are now tied to a laboratory-defined batch. The GFAA portion contains similar editorial and technical changes. Technical changes also included specifications for filter paper. The calibration requirement for three standards has been clarified by discussing it in the calibration section as well as the QC section.

TABLE 1B. Updated ASTM Methods

Metals Part 4		
Method	**Analyte**	**Comment**
D4190-15	Metals: Al, Be, Bo, Cd, Cr, Co, Fe, Pb, Ni, V, Zn	Added a requirement to run at least four calibration standards for all metals, as opposed to running four standards for only lithium to demonstrate linearity.
D4382-18	Barium	Changed the description of the hot block digester equipment. The new version specifies the capability to heat samples between 65 and 95 degrees C, instead of "approximately 95 degrees C." That change recognizes the operational characteristics of hot block digesters that will experience a temperature drop below 95 degrees when samples are added. This should not adversely affect use of this method.
D511-14 (A, B)	Ca, Mg	Added specifications for filter paper.
D5257-17	Chromium, hexavalent	Added a few additional warnings or recommendations.

TABLE 1B. Updated ASTM Methods

Metals Part 5		
Method	**Analyte**	**Comment**
D5673-16	Gold	Gold was added to the list of target analytes. Some of the changes address the analysis of gold.
D6919-17	NH4, Ca, Mg, K, Na	No procedural changes.
D858-17 (A–C)	Manganese	No procedural changes.
D859-16	Silica	No procedural changes.

TABLE 1B. Updated ASTM Methods

Organics and Other		
Method	**Analyte**	**Comment**
D1252-06 (A, B) (12)	Chemical Oxygen Demand	No procedural changes.
D1253-14	Chlorine, residual	No procedural changes.
D1783-01 (A, B) (12)	Phenols	No procedural changes.
D4839-03 (17)	Total Organic carbon	No procedural changes.
D7573-09 (17)	Total Organic carbon	No procedural changes.

New Footnotes 79-83

79. I-2057-85 U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chap. A11989, Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, 1989.

80. Methods I-2522-90, I-2540-90, and I-2601-90 U.S. Geological Survey 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.

81. Method I-1472-97, U.S. Geological Survey Open-File Report 98-165, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory–Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments, 1998.

82. FIAlab Instruments, Inc. Method FIAlab 100, "Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Fluorescence Detector Analysis", April 4, 2018, FIAlab Instruments, Inc.

83. MACHEREY-NAGEL GmbH and Co. Method 036/038 NANOCOLOR® COD LR / HR, "Spectrophotometric Measurement of Chemical Oxygen Demand in Water and Wastewater", Revision 1.5, May 2018, MACHEREY-NAGEL GmbH and Co. KG.

New Footnote 84

Standard Methods[84]

Please refer to the following applicable Quality Control Sections:

- Part 2000, Physical and Aggregate Properties 2020;
- Part 3000, Metals, 3020;
- Part 4000, Inorganic Nonmetallic Constituents, 4020;
- Part 5000, and Aggregate Organic Constituents, 5020.

These Quality Control Standards are available for download at www.standardmethods.org at no charge.

New Footnote 85

BOD5 5210B-16[85] **CBOD5 5210B-16[85]**

Each laboratory may establish its own control limits by performing at least 25 glucose-glutamic acid (GGA) checks over several weeks or months and calculating the mean and standard deviation. The laboratory may then use the mean ± 3 standard deviations as the control limit for future GGA checks. However, GGA acceptance criteria can be no wider than 198 ± 30.5 mg/L for BOD5. GGA acceptance criteria for CBOD must be either 198 ± 30.5 mg/L, or the lab may develop control charts under the following conditions:

- Dissolved oxygen uptake from the seed contribution is between 0.6 – 1.0 mg/L.
- Control charts are performed on at least 25 GGA checks with three standard deviations from the derived mean.
- The RSD must not exceed 7.5%.
- Any single GGA value cannot be less than 150 mg/L or higher than 250 mg/L.

New USGS Methods

Method	Technology	Analytes
I-2057-85	Anions, ion-exchange chromatographic, automated	Br, Cl, F, No3, NO2, o-PO4, S2, SO4
I-2540-90	Nitrogen, nitrite, colorimetry, diazotization, automated-segmented flow	nitrite.
I-2601-90	Phosphorus, orthophosphate, colorimetry, phosphomolybdate, automated-segmented flow	orthophosphate.
I-4472-97	Metals, Acid Digestion, Whole- Water Recoverable, inductively coupled plasma-mass spectrometry	Al, Sb, Ba, Be, Cd, Cr, Co, pb, Mn, Mo, Ni, Se, Ag, Se, Th, Zn
I-2522-90	colorimetry, salicylate-hypochlorite, automated-segmented flow	Ammonia

Other New Methods

Method Number	Method Name
FIAlab Method 100	Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Fluorescence Detector Analysis
MACHEREY-NAGEL GmbH and Co. Method 036/038 NANOCOLOR® COD LR / HR	Spectrophotometric Measurement of Chemical Oxygen Demand in Water and Wastewater

Changes to Table 1C

- Revised Method
  - ASTM D7065-17, nonylphenol, bisphenol A, p-tert-octylphenol, nonylphenol monoethoxylate, nonylphenol diethoxylate, by GC/MS.
- New Methods
  - USGS O-4127-97, Volatile Organic Compounds by GC/MS
  - USGS O-4127-97, Heat Purgeable and Ambient PurgeableVolatile Organic Compounds by GC/MS
- New Footnotes

13. Method O-4127-96, Determination of 86 volatile organic compounds in water by gas chromatography/mass spectrometry, including detections less than reporting limits,1998.
14. Method O-4436-16, Determination of heat purgeable and ambient purgeable volatile organic compounds in water by gas chromatography/mass spectrometry, 2016.

Table II: Holding Times and Sample Preservation

- Bacteria
  - Updated parameter numbers to match changes in Tables 1A and 1H.
- Cyanide
  - Updated Footnote 6 for the preservation and holding time requirements for cyanide to cite the latest version of ASTM method D7365-09a that was reapproved in 2015
- Chlorinated Hydrocarbons
  - Added Parameter 73, Hexachloroethane
- Volatile Halogenated Organics
  - Added HCl as optional preservative except for 2-CEVE with 14 day holding time
- Dioxins
  - Indented matrices under this category to remove confusion.

Method Modifications: 136.6

- New language on microwave digestion for metals
  - When analyzing metals by inductively coupled plasma-atomic emission spectroscopy, inductively coupled plasma-mass spectrometry, and stabilized temperature graphite furnace atomic absorption, closed-vessel microwave digestion of wastewater samples is allowed as an alternative heating source for EPA Method 200.2, "Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements" for the following elements: aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, selenium, silver, sodium, thallium, tin, titanium, vanadium, zinc, provided the performance specifications in the relevant determinative method are met. (Note that this list does not include Mercury.) Each laboratory determining total recoverable metals is required to operate a formal quality control (QC) program. The minimum requirements include initial demonstration of capability, method detection limit (MDL), analysis of reagent blanks, fortified blanks, matrix spike samples, and blind proficiency testing samples, as continuing quality control checks on performance. The laboratory is required to maintain performance records on file that define the quality of the data generated.

Summary of Proposed Changes to Part 136

- Updated many methods to current versions
- Corrected technical errors
- Provided additional clarification

SUMMARY

- Not as dramatic as the 2017 rule
  - Most of this just adds revised methods, corrects problems and increases flexibility

Implementation Options

- Do nothing until your State requires this.
- A user may, on a facility-by-facility basis, seek limited use approval from their Regional ATP Coordinator. EPA is encouraging States and Regions to allow for the use of these methods provided that the requirements for establishing equivalent performance at 136.6 are met. (from 2017 MUR)