

Methods Update Rule

FSEA Fall Meeting

October 28, 2010

Jerry L. Parr

Catalyst Information Resources

817-598-1177

catalyst@eazy.net

www.CatalystInfoResources.com

Methods Update Rule



- Proposed September 23, 2010
- New methods
- Updated versions of approved methods
- Revised method modification and analytical requirements
- Clarifications and corrections
- Changes to sample collection, preservation, and holding time requirements
- Minimum QC requirements

Comments due November 22, 2010

Regulations Affected



- **Part 423:** Steam Electric Power NPDES
 - Revise definitions related to residual chlorine
- **Part 430:** Pulp and Paper NPDES
 - Remove Methods 1650 and 1653
- **Part 435:** Oil and Gas NPDES
 - Method revisions and corrections
- **Part 136:** Wastewater Methods
 - **Many, many, many changes**
- **Part 260:** RCRA Methods
 - Update 1664A to 1664B

Changes to Part 136



- New EPA Methods
- Updated EPA Methods
- New and Updated Standard Methods
- New and Updated ASTM Methods
- > 250 New Analytes
- New table for microbiology in ambient water
- Table II: Preservation & Holding Time
- Sections 136.4 and 136.5 on ATP
- Section 136.6, Method Modifications
- New Section 136.7 on minimum QC
- Remove Appendices A (600 methods) and C (200.7)
- Revise Appendix D (metals P/A data)

New EPA Methods



- **200.5** Trace Elements by Axially Viewed ICP-AES
- **525.2** Organics by GC/MS (Table 1G only)
- **608.1** Organochloride Pesticides. (Table 1G only)
- **608.2** Organochlorine Pesticides. (Table 1G only)
- **614** Organophosphorus Pesticides. (Table 1G only)
- **614.1** Organophosphorus Pesticides (Table 1G only)
- **617** Organohalide Pesticides and PCBs. (Table 1G only)
- **619** Triazine Pesticides. (Table 1G only)
- **622** Organophosphorus Pesticides (Table 1G only)
- **622.1** Thiophosphate Pesticides. (Table 1G only)
- **632** Carbamate and Urea Pesticides (Table 1G only)
- **1614A** Brominated Diphenyl Ethers by HRGC/HRMS.
- **1668C** Chlorinated Biphenyl Congeners by HRGC/HRMS.
- **1627** Prediction of Mine Drainage Quality.

A Closer Look: Methods 1614A and 1668C



- 49 PDBEs
- 209 PCB Congeners
- Listed in Table 1C as:
 - 119. Polybrominated diphenyl ethers (PBDEs) 49 congeners.
 - 120. Polychlorinated biphenyls (PCBs) 209 Congeners.

A Closer Look: Method 1627



- Simulated weathering test that provides information to predict the quality of mine drainage from coal mining operations or weathering
- Listed in Table 1B as parameter:
 - 76. Acid Mine Drainage

Revised/Updated EPA Methods



- 1664B Oil and Grease (HEM and SGT-HEM)
- 624 Add acrolein and acrylonitrile as approved analytes
- 1622 Cryptosporidium
- 1623 Giardia
- 1103.1 E. coli
- 1106.1 Enterococci
- 1600 Enterococci
- 1603 E. coli
- 1680 Fecal Coliform
- 1650 121. Adsorbable Organic Halides
- 1653 122. Chlorinated Phenolics

New Analyte

New Analyte

A Closer Look: Methods 1622 and 1623



- **Update to 2005 version**
 - flexibility to choose among several types of filters, quality controls, and stains,
 - clarification on measuring sample temperatures, quality control sample requirements and use of quality control sample results,
 - minimizing carry-over debris,
 - analyst verification procedures, and
 - sample condition criteria upon receipt.
- **Change preservation to 1-10 degrees C**

Methods 1103.1, 1106.1, 1600, 1603, and 1680



- **Minor technical corrections, e.g.**
 - tryptone broth should be tryptone water
 - positive control organism for the cytochrome oxidase reagent has been changed to *P. aeruginosa* from *E. faecalis*,
 - negative control organism for Simmons citrate agar has been changed to *S. flexneri* from *E. coli*

Standard Methods



- Generally, only most recent version will now be approved
 - 17th, 18th, 19th, etc. no longer approved
 - Method approval is shown by the year, not the edition
- New Methods
- Updated Methods
- New method and a new analyte: 17A. Chlorine - Free available

New and Updated Standard Methods



- 5520 B-2001 and 5520 F-2001 Oil and Grease.
 - SM 5520 G-2001 not approved because it allows use of a co-solvent, such as acetone.
- 4500-NH₃ G-1997 Ammonia (as N) and TKN
- 4500-B B-2000 Boron.
- 4140-1997 Inorganic Ions
- 3114 C-2009 Arsenic and Selenium.
- 3111 E-1999 Aluminum and Beryllium.
- 5220 B-1997 Chemical Oxygen Demand.
- 4500 NORG D-1997 Kjeldahl Nitrogen - Total.
- 4500 P G and 4500 P H-1999 Phosphorus.
- 4500 P E and 4500 P F-1999 Phosphorus.
- 4500 O B, D, E and F-2001 Oxygen.
- 4500 O D-2001 Oxygen.
- 4500 O E-2001 Oxygen.
- 3500 K C-1997 Potassium.
- 2540 E-1997 Residues – Volatile.
- 4500 SiO₂ and 4500 SiO₂ F- 1997 Silica.
- 4500 SO₄ C, D, E, F and G-1997 Sulfate.
- 4500 S²⁻ B-2000 and C-2000, Sulfide.

New and Updated ASTM Methods



- D2036, D6888, D7284, and D7511 Total Cyanide
- D888 Dissolved Oxygen
- D7573 Total Carbon and Organic Carbon.

ASTM New Analytes and Methods



- D4282 and D7237
 - D7065, D7574, & D7485
 -
 -
 -
 -
- 24A. Free Cyanide
 - 114. Nonylphenol
 - 115. Bisphenol A
 - 116. p-tert-Octylphenol
 - 117. Monoethoxylate
 - 118. Nonylphenol Diethoxylate

More New Methods



- SM 3125-2009 ICP/MS for 24 metals
- ASTM 1976-2007 ICP/AES for 25 metals

Not discussed in preamble

ICP/AES and ICP/MS for Additional Metals

- Gold by ICP/MS (4 methods)
- Iridium by ICP/MS (SM 3125)
- Magnesium by ICP/MS (4 methods)
- Mercury by ICP/AES and ICP/MS (4 methods)
- Palladium by ICP/MS (SM 3125)
- Phosphorous by ICP/AES (3 methods)
- Platinum by ICP/MS (SM 3125)
- Potassium by ICP/MS (4 methods)
- Rhodium by ICP/MS (SM 3125)
- Rhodium by ICP/MS (SM 3125)
- Silica by ICP/MS (4 methods)
- Sodium by ICP/MS (4 methods)
- Tin by ICP/MS (4 methods)
- Titanium by ICP/MS (4 methods)

Not discussed in
preamble

ASTM - Oil and Grease Methods



- **D7066 and D7575 not included**
 - Do not use n-hexane
 - Other significant changes from 1664
 - TPH is not an analyte in Part 136

New Alternate Test Procedures



- Hach Method 10360 Luminescence Measurement of Dissolved Oxygen (LDO[®]),
- In-Situ Incorporated's
 - Method 1002-8 Dissolved Oxygen (DO),
 - Method 1003-8 BOD, and
 - Method 1004-8 CBOD,
- Mitchell Methods M5271 and M5331 for turbidity;
- Thermo Scientific's Method AQ4500 for turbidity;
- Systea Scientific, LLC's Systea Easy (1-Reagent) Nitrate.

Clarifications and Corrections



- Grab samples must be filtered within 15 minutes for o-PO₄ Preamble only
- Fecal coliform, total coliform, and fecal streptococcus methods added to Table 1H
- Other minor corrections

Holding Times and Sample Preservation



- Information in this table takes precedence over instructions provided in specific methods or elsewhere unless a party documents the acceptability of an alternative to the Table II instructions. The nature, timing and extent of the required documentation (i.e. how to apply and review as well as the amount of supporting data) are left to the discretion of the permitting authority (State Agency or EPA Region) or other authority and may rely on instructions, such as those provided for method modifications at 136.6.
- Examples provided:
 - 24-hour BOD
 - Cyanide

Holding Times and Sample Preservation



- *E. Coli* and *Enterococcus*
 - Change from 2 hours to 8 hours
- Cyanide
 - Footnotes 5 and 6 extensively rewritten (shortened) to reference ASTM Methods and allow analyst flexibility
- WET
 - Samples cannot be frozen
 - Do not need to be 0-6 C if analyzed on day of collection
 - Hold time only refers to first use

Alternate Test Procedures



- **136.4: Nationwide**

- Application to National Coordinator
- Provide a detailed description of the proposed procedure.
- Provide comparability data
- Procedure may be used for limited use prior to regulation

- **136.5: Limited**

- Application to Regional Coordinator
- Provide justification
- Provide a detailed description of the proposed procedure.
- Demonstrate applicability to specific effluents

Method Modifications: 136.6



- Extensively rewritten with more examples
- 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

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.

New 136.7: Required Quality Control



- **Mandatory for all methods**
- **12 Essential QC Checks**
 - (1) Demonstration of Capability (DOC);
 - (2) Method Detection Limit (MDL);
 - (3) Laboratory reagent blank (LRB), also referred to as method blank;
 - (4) Laboratory fortified blank (LFB), also referred to as a spiked blank, or laboratory control sample (LCS);
 - (5) Matrix spike, matrix spike duplicate, or laboratory fortified blank duplicate (LFBD) for suspected difficult matrices;
 - (6) Internal standards, surrogate standards (for organic analysis) or tracers (for radiochemistry);

12 QC Checks (the last 6)



- (7) Calibration (initial and continuing), initial and continuing performance (ICP) solution 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 analyses);
- (10) QC acceptance criteria;
- (11) Definitions of a batch (preparation and analytical); and
- (12) Specify a minimum frequency for conducting these QC checks.

Changes to Appendix D



- Precision and Accuracy Data for EPA AA Methods
- Almost all methods were deleted in 2007 MUR
- Proposed rule would remove all Appendix D data except for:
 - 279.2, Thallium
 - 289.2, Zinc

Changes to Part 423



- NPDES Regulations for power plants
- Revise definitions for residual and free chlorine
 - 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.
 - Free available chlorine means the value obtained using any of the chlorine-free available methods in Table IB.

Changes to Part 430



- NPDES Regulations for pulp and paper plants
- Remove Methods 1650 and 1653 for adsorbable organic halides (AOX) and chlorinated phenolics
- Add adsorbable organic halides (AOX) and chlorinated phenolics as analytes 121 and 122 in Table 1C

Analyte 122: Chlorinated Phenolics



- Trichlorosyringol
- 3,4,5-Trichlorocatechol
- 3,4,6-Trichlorocatechol
- 3,4,5-Trichloroguaiacol
- 3,4,6-Trichloroguaiacol
- 4,5,6-Trichloroguaiacol
- 2,4,5-Trichlorophenol
- 2,4,6-Trichlorophenol
- Tetrachlorocatechol
- Tetrachloroguaiacol
- 2,3,4,6-Tetrachlorophenol
- Pentachlorophenol

Changes to Part 435



- NPDES Regulations for offshore oil and gas wells
- Remove methods and create *Analytic Methods for the Oil and Gas Extraction Point Source Category*
- Incorporate additional QA procedures in the marine anaerobic biodegradation analytic method
- Correct some erroneous references and omissions in the method for identification of crude oil contamination
- Add a schematic flow diagram for qualitative identification of crude oil

Methods for Offshore Oil and Gas



- 1617 Static Sheen Test
- 1619 Drilling Fluids Toxicity Test
- 1646 Procedure for Mixing Base Fluids With Sediments.
- 1647 Degradation of Non Aqueous Base Fluids in a Marine Closed Bottle Biodegradation Test System:
- 1655 Crude Oil Contamination in Non-Aqueous Drilling Fluids by GC/MS.
- 1670 Detection of Oil Contamination in Non-Aqueous Drilling Fluids (NAF).
- 1674 Non- Aqueous Drilling Fluid (NAF) Base Fluid from Drill Cuttings

SUMMARY



- This is a PROPOSED rule
 - It may take 2-3 years to finalize
 - Expect some changes, but be prepared
 - Send in your comments
-
- http://water.epa.gov/scitech/swguidance/methods/update_index.cfm

Jerry L. Parr

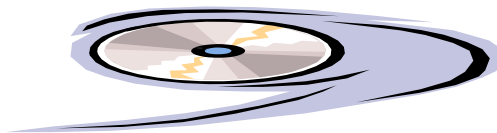
 Catalyst Information Resources

The Information Resource for Environmental Professionals

817-598-1155

catalyst@eazy.net

www.CatalystInfoResources.com



LABFACTS

- Over 3400 Documents
 - ▶ Redline version of method tables
- Free Trial Copy on request

3. Acrolein	GC	603
	GC/MS	624 ⁴ , 1624B