



**Methods Update Rule
Information
40 CFR Parts 122, 136,
141, 143, 430, 455 & 465**

**The NELAC Institute
Denver Assessor's Forum 1/07**

Time Line

**1. August 18, 2003 & April 6, 2004 –
the proposed method changes were
published for comment.**

**2. July 21, 2006 – Administrator signed
the final rule. Pre-publication rule**

<http://www.epa.gov/waterscience/methods/update2003/index.html>

**3. Forthcoming for compliance purposes
is the published version on GPO's
website**

**4. 30 days after publication, the new rule
would be in effect**

**The information on next 27 slides
provided by:**

Jerry L. Parr

Catalyst Information Resources

817-598-1177

catalyst@eazy.net

www.CatalystInfoResources.com

New Chemical Test Methods for CWA

- **ASTM D6508**, Dissolved Inorganic Anions by Capillary Ion Electrophoresis,
- **QuikChem Method 10-204-00-1-X**, Cyanide using MICRO DIST and flow injection analysis,
- **Kelada-01**, Automated Methods for Total Cyanide, Acid Dissociable Cyanide, and Thiocyanate,
- **Method CP-86.07**, Chlorinated Phenolics by In situ Acetylation and GC/MS (Part 430),
- **EPA 245.7**, Mercury by Cold Vapor Atomic Fluorescence Spectrometry,
- **SM 4500-Cl**, Chlorine by Low Level Amperometry,
- **ASTM D6888-04**, Available Cyanide by Ligand Exchange-FIA,
- **ASTM D 6919-03**, Cations and Ammonium in by IC,
- **SM 4500-Cl-D**, Chloride by Potentiometry,

New Chemical Test Methods for CWA (Cont.)

- **ASTM D512-89**, Chloride by Ion Selective Electrode,
- **SM 4500-CN-F**, Cyanide by Ion Selective Electrode,
- **ASTM D2036-98 A**, Cyanide by Ion Selective Electrode,
- **SM 4500-S2-G**, Sulfide by Ion Selective Electrode,
- **ASTM D4658-03**, Sulfide by Ion Selective Electrode,
- **SM 4500-NO3-D**, Nitrate by Ion Selective Electrode,
- **ASTM D99-003**, Free Chlorine by Color Comparison Test Strip,
- **Method OIA-1677**, DW Available Cyanide by Ligand Exchange—FIA,
- **Radium-226 and 228**, by Gamma Spectrometry, and
- **EPA 327.0**, Chlorine Dioxide by Colorimetry

Re-proposed Chemical Test Methods for CWA

- First Proposed in 1994
 - **200.2**, Total Recoverable Elements Digestion
 - **200.8**, Metals by ICPMS
 - **200.9**, Metals by Stabilized Temperature GFAA
 - **218.6**, Hexavalent Chromium by IC
 - **300.0**, Inorganic Anions by IC
 - **353.2**, Nitrate and Nitrite by Colorimetry
 - Revisions to 180.1(2), 200.7(4.4), 245.1(3.0), 335.4 (1.0), 350.1(2), 351.2(2), 353.2(2), 365.1(2), 375.2 (2), 410.4(2), and 420.4(1).
- Equivalent ASTM and SM methods also approved

Updated Versions of Current CWA Methods

- An errata sheet for the WET manuals (typographical errors)
- ASTM methods
- Standard Methods
- Methods published in the 16th edition of Official Methods of Analysis of AOAC International, 1995

CWA Allowable Method Modifications

- Replace the mercury catalyst with copper sulfate in TKN methods-based on comments, both options are allowed.
- Approve the use of styrene divinyl benzene beads and Hach StablCal as alternatives to the formazin standard for Turbidity
- Allow the use of capillary GC columns for Methods 601-613, 624, 625, and 1624B (new RT table documented)

Revised CWA Method Requirements

- Clarify that analysts need only meet method performance requirements for target analytes.
- Allow method modifications without prior EPA approval by passing QC checks.
- Clarify that results be reported to the level specified in the method or required in the permit, whichever is lower.

Withdrawal of CWA Methods

- Delete Methods 612 and 625 for dichlorobenzenes
- Withdraw approval for all oil and grease methods that use Freon-113
- Withdraw > 100 methods in MCAWW

Side Note Regarding Freon

- Essential Laboratory Use Rule (2/11/02 Federal Register)
 - Three-year exemption for the use of Freon in environmental test methods, until 12/31/05
 - Rule does not apply to laboratories!
- EPA planning to remove 413.1 from Part 136; 413.2 and 418.1 were never promulgated
- EPA Clarification Memo, 12/30/05

Sampling and Preservation

- Change 4° C to 0-6° C
- Change HT for Cr⁺⁶ to 28 days
- Various changes for mercury
- No acid preservation for metals in the field (except Hg)
- HT starts at end of composite period
- Other minor changes

Side Note on Preservation

- New DOT rule prohibits use of nitric acid in empty containers
- Emergency exemption to rule possible

Regulations Changed

- Part 122: NPDES Permits
 - Minor clarifications
- Part 136: Wastewater Methods
 - **Many, many, many changes**
- Part 141: Drinking Water
 - Conforming changes
- Part 143: Drinking Water
 - Conforming changes
- Part 430: Pulp & Paper NPDES
 - Approve method for chlorinated phenolics
- Part 455: Pesticide Manufacturing NPDES
 - Move Table 7 to Part 136
- Part 465: Coil Coating NPDES
 - Removal of oil and grease

Part 136

- Table 1A: Microbiologicals (SM only)
- Table 1B: Inorganics/Metals
- Table 1C: Organics
- Table 1D: Pesticides (SM & ASTM only)
- Table 1E: Radiochemistry (SM & ASTM only)
- Table 1F: Pharmaceutical Pollutants
- Table 1G: Pesticide Active Ingredients
- Table II: Preservation & Holding Time
- Section 136.6

Changes to Part 136, Table 1B EPA Methods

- Deleted 52 wet chem methods
- Deleted 53 AA methods
- Approved 7 new EPA methods
- Approved 10 revisions to existing EPA methods

Table IB: Deleted CWA WetChem Methods

- Alkalinity: **305.1, 310.1**
- Ammonia: **350.2, 350.3**
- BOD: **405.1**
- Bromide: **320.1**
- COD: **410.1, 410.2**
- Chloride: **325.1, 325.2, 325.3**
- Chlorine: **330.1, 330.2, 330.3, 330.4, 330.5**
- Chromium VI: **218.4**
- Color: **110.1, 110.2, 110.3**
- Cyanide: **335.1, 335.2, 335.3**
- Fluoride: **340.1, 340.2, 340.3**
- Hardness: **130.1**
- pH: **150.1**
- TKN: **351.3, 351.4**
- NO₃-NO₂: **353.1, 353.3**
- NO₂: **354.1**
- Oil & grease: **413.1**
- TOC: **415.1**
- o-PO₄: **352.2**
- DO: **360.1, 360.2**
- Phosphorous: **365.2**

Table IB: Deleted CWA WetChem Methods (cont.)

- **TS: 160.3**
- **TDS: 160.1**
- **TSS: 160.2**
- **SS: 160.5**
- **Silica: 370.1**
- **Sulfate: 375.1, 375.3, 375.4**
- **Sulfide: 376.1, 376.2**
- **Sulfite: 377.1**
- **Surfactants: 425.1**
- **Temperature: 170.1**

Deleted CWA EPA AA Methods

- Aluminum: 202.1, 202.2
- Antimony: 204.1, 204.2
- Arsenic: 206.2, 206.3, 206.4
- Barium: 208.1, 208.2
- Beryllium: 210.1, 201.2
- Boron: 212.3
- Cadmium: 213.1, 213.2
- Calcium: 215.1, 215.2
- Chromium: 218.2, 218.2, 218.3
- Cobalt: 219.1, 219.2
- Copper: 220.1, 220.2
- Gold: 213.1
- Iridium: 235.1
- Iron: 236.1, 236.2
- Lead: 239.1, 239.2
- Magnesium: 242.1
- Manganese: 243.1, 243.2
- Molybdenum: 246.2, 246.2
- Nickel: 249.2, 249.2
- Osmium: 252.1
- Palladium: 253.1
- Platinum: 255.1
- Potassium 258.1

Deleted CWA EPA AA Methods (cont)

- Rhodium: 265.1
- Ruthenium: 267.1
- Selenium: 270.2
- Silver: 270.1, 270.2
- Sodium: 273.1
- Thallium: 279.1
- Tin: 282.1, 282.2
- Titanium: 283.2
- Vanadium: 286.1, 286.2
- Zinc: 289.1

New CWA EPA Methods

- **200.8:** ICP MS
- **200.9:** SFGTAA
- **218.6:** Cr6 by ion chromatography
- **245.7:** Hg by CFAFS
- **300.0:** Anions by ion chromatography
- **300.1:** Anions by ion chromatography
- **335.4:** Cyanide

Method 200.8, Rev.4.4-1998

- Al
- Sb
- As
- Ba
- Be
- Cd
- Cr
- Co
- Cu
- Fe
- Pb
- Mn
- Mo
- Ni
- Se
- Ag
- Tl
- V
- Zn

Method 200.9, Rev. 2.2- 1994

- Al
- Sb
- As
- Be
- Cd
- Cr
- Co
- Cu
- Fe
- Pb
- Mn
- Ni
- Se
- Ag
- Tl
- Sn
- Zn

Anions by Ion Chromatography

- **300.0, 2.1**

- Bromide
- Chloride
- Fluoride
- NO₃
- NO₃-NO₂
- NO₂
- o-PO₄
- Sulfate

- **300.1, 1.0**

- Bromide
- Chloride
- Fluoride
- NO₃
- NO₃-NO₂
- NO₂
- o-PO₄
- Sulfate

Updated Revisions of Current EPA CWA Methods

- Turbidity: **180.1**, 2.0
- ICP/AES: **200.7**, 4.4
- Mercury: **245.1**, 3.0
- Ammonia: **350.1**, 2.0
- TKN: **351.2**, 2.0
- NO₃-NO₂: **353.2**, 2.0
- NO₂: **353.2**, 2.0
- o-PO₄: **365.1**, 2.0
- Phosphorous: **365.1**, 2.0
- Sulfate: **375.2**, 2.0
- COD: **410.4**, 2.0

Part 136, Table 1C: Organics

- Delete methods 612 and 625 for dichlorobenzenes. Methods 624 and 1625 should be used.
- Approve updated versions of SM, ASTM, etc.
- Add footnotes indicating EPA QC requirements apply to non-EPA methods

Part 136, Table 1G: Methods for PAI

- List of 93 non-routine pesticides with method references
- Table was in Part 455
- Methods include obscure methods (e.g., 1656, 1657) as well as 500 series methods

Part 136, Table II

Holding Times & Preservation

- 4°C changed to < 6°C
- Analyze immediately changed to 15 minutes
- No acid preservation for metals in field
 - Must wait 24 hours after adding acid
 - Does not apply to Hg
- Cr+6: 28 day HT, if sample buffered to pH 9.3 to 9.7
- HT starts at end of composite period
- Extensive requirements for cyanide
- Other minor changes- read carefully!

136.6: Method Modifications

- Analysts may modify methods!!!
 - Not change the “chemistry”
 - Excludes “method-defined” analytes
- Requirements for modifications:
 - Initial DOC (IPR)
 - On-going QC
 - Verification in wastewater matrices
- Reference to **Pumpkin Book**

Impact of New Rule

- Deleted EPA Methods
 - Permits
 - Accreditation
 - LIMS
 - Reports
 - Operational changes
 - Etc.
- Implementation of 136.6



Assessor's Concerns

- 30 days after publishing isn't enough time for labs to begin new methods, update SOPs, complete IDOCs and have the new methods in their scope of accreditation.
- Accreditation Programs also have to place the new methods in their rules.

Assessor's Concerns

- What about old methods in older NPDES permits?
- NOTE: Richard Reding of EPA provided an e-mail on 12/26/06 stating the following:
... What about methods withdrawn from part 136 for CWA monitoring by the final Methods Update Rule? The primacy authority should allow use of methods in the permit for the life of the permit unless the authority exercise permit reopener procedures. Also this final rule does not withdraw any ATP approval that is tied to one of the withdrawn methods. All or most of the withdrawn EPA methods have equivalent part 136 methods published by organizations, such as ASTM or Standard Methods. We expect formal publication of the rule in February.

Assessor's Concerns

- Some states want to retain the EPA residue methods that were withdrawn because the SM reference requires using a pipet for sample volume, which would introduce more error, in using several pipets for the full volume or use of a wide bore pipet that would prefilter a sample, thus making it unrepresentative.
- NOTE: Arizona has received an e-mail from Richard Reding on 10/31/06 stating that the use of a Class A graduated cylinder is an acceptable method modification to the SM residue methods requirement of using a pipet for sample volume.

Assessor's Concerns

- There was an approval to remove the mercury catalyst for TKN but still allows it for Phosphorus determination.
- NOTE: Lem Walker provided an e-mail on 12/19/06 stating the following:

“As written, 351.2 Rev 2 specifies the use of a mercury catalyst in 7.2 and 7.3. Notes 1 and 2 under 7.3 and 7.4 offers information about but does not directly require the use of a alternative mercury-free digestion solution. Since EPA 365.4 (issued 1974) is still listed as an approved method for Total P and the digestion using mercury catalyst is the same as in 351.2 Rev 2 both TKN and Total P could still be analyzed from a single digestion.

”

New Chemical Test Methods for SDWA

- **D6508, Rev. 2**, Dissolved Inorganic Anions by Capillary Ion Electrophoresis,
- **ASTM D6888-04**, Available Cyanide by Ligand Exchange-FIA,
- **OIA-1677**, Available Cyanide by Ligand Exchange-FIA,
- **ASTM D 6919-03**, Cations by IC,
- **300.1, Rev. 1.0**, Chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate by IC,
- **552.3, Rev. 1.0**, Dalapon,
- **Ra-226 & Ra-228 by Gamma-ray Spectrometry using HPGE of Ge(Li) detectors**, Rev. 1.2,
- **D99-003, Rev. 3**, Free Chlorine ITS test strips,
- **327, Rev.1.1**, Chlorine dioxide residuals

SDWA Allowable Method Modifications

- Approve the use of styrene divinyl benzene beads and stabilized formazin as alternatives to the formazin standard for Turbidity
- Allow the use of a 450-W UV lamp in the Kelada Method-01 for Cyanide
- Allow the use of Syngenta method AG-625, with modified immunoassay testing product by Beacon Analytical System, under certain conditions.

Footnote Clarification

- Revises Footnote 8 to table in paragraph (a)(1) in 141.74, correcting the A-1 broth holding time specified in the footnote to match the 7-day hold time specified in SM 9221 E (fecal coliforms).

Presented By:

Barbara A. Escobar

Environmental Program Manager

ADHS Office of Laboratory Services

520-903-1620 or escobab@azdhs.gov