

The 201x Method Update Rule

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Disclaimers



- This presentation represents the professional opinion of Jerry Parr and has not been reviewed or endorsed by The NELAC Institute
- There was a lot of information reviewed, and some errors may exist. **Read the Rule, the Methods, and the MDL procedure!**



2017 Methods Update Rule



- Finalized on December 2016
- Withdrawn March 2017
- **Effective summer 2017?**
- Updated EPA Methods
- New and Updated Standard Methods, ASTM methods and methods from other sources
- Changes to sample preservation and holding times for microbiology
- Revised MDL Procedure
- Other “Technical Corrections”

Reading the Federal Register



- Preamble
 - Introductory Material
 - **Summary and Changes**
 - ✦ Some changes are not mentioned
 - Statutory Material
- The Rule
 - Only shows changes, except tables that do not
- The Docket

The Docket



- www.regulations.gov
- Docket ID No. EPA–HQ– OW–2014–079
- The new methods
- The WET errata sheet
- The 300.1 errata sheet
- Response to Comments document

This will not exist until the rule is final

Changes to Part 136



- 136.2 Definitions (Director)
- 136.3 Test Procedures
 - 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
- 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

Tables 1 A and 1H. Microbiology



Table 1 A

- Updated methods
 - SM 9221 B, C, E, F -06, (Coliform, fecal and total; *E. coli*)
 - SM 9222 B, C, G-06 (Coliform)
 - SM 9223-04 (*E. coli*)
 - SM 9230 B, C-07 (Fecal streptococci, Enterococci)
 - Colilert 18 (Fecal coliform)
- Updated EPA Methods
 - 1600, 1603, 1680, 1682
 - WET methods

Table 1 H

- Updated versions
 - SM 9222B-06
 - SM 9222D and G-06
 - SM 9213-07
- Updated EPA Methods
 - 1600, 1603, 1622, 1623

Changes in Micro Methods



- 9222B: Allow use of humidified incubator and added Note that 5 typical and atypical colonies needed for ID.
- 9222D: Allow use of dry circulating incubator ~~and same Note as above~~
- 9222D: Added footnote 30: On a monthly basis, at least ten blue colonies from the medium must be verified using Lauryl Tryptose Broth and EC broth, followed by count adjustment based on these results; and representative non-blue colonies should be verified using Lauryl Tryptose Broth. Where possible, verifications should be done from randomized sample sources.
- Colilert 18: Increased incubation temperature requiring waterbath incubator for Fecal Coliforms.

Methods 1600, 1603, 1680 and 1682 (2014)



Minor technical corrections

- 1600: Change the negative control for brain heart infusion broth from *E. coli* to *Enterobacter aerogenes*.
- 1603: Change the number of colonies on a countable plate from 20-60 to 20-80 colonies. Add “Sample volumes of 1-100 mL are normally tested at half-log intervals (e.g., 100, 30, 10, and 3 mL).”
- 1680: Change “The predominant fecal coliform is *E. coli*.” to “can be *E. coli*.”
- 1682: In Table 2, the acceptance criteria should be “Detect – 254%” and “Detect – 287%” and in Table 9, the spiked *Salmonella* criteria should be “ 3.7×10^8 CFU/mL.”

Updated methods in Docket

WET Errata



- **Many changes**
 - Some trivial such as “minimum **test** acceptability criteria.”
 - Some significant such as “Replace the graphs in Figure 1 with log scale graphs.”
- **Errata sheet only available in Docket**
 - There was a different undated errata sheet in the OST methods website but it appears to have been removed

Table 1 B. Metals and Wet Chem



- New Methods
- Updated Methods
- New and revised footnotes

Redline version available on request

Parameter	Methodology ⁵⁸	EPA ⁵²	Standard methods	ASTM	USGS/AOAC/Other
1. Acidity, as CaCO ₃ , mg/L	Electrometric endpoint or phenolphthalein endpoint		2310 B-11	D1067-11	I-1020-85 ²
2. Alkalinity, as CaCO ₃ , mg/L	Electrometric or Colorimetric titration to pH 4.5, manual		2320 B-11	D1067-11	973.43 ³ I-1030-85 ²
	Automatic	310.2 (Rev 1974)			I-2030-85 ²

Table 1B. Updated Standard Methods



- 2120 B, F-11
- 2130 B-11
- 2310 B-11
- 2320 B-2011
- 2340 B, C-11
- 2340 C-11
- 2510 B-11
- 2540 B, C, D, E, F-11
- 2550 B-10
- 3111 B, C, D, E-11
- 3112 B-11
- 3113 B-10
- 3114 B, C-11
- 3120 B-11
- 3125 B-11
- 3500-Al B-11
- 3500-As B-11
- 3500-Ca B-11
- 3500-Cr B, C-11
- 3500-Cu B, C-11
- 3500-Fe B-11
- 3500-K B,C-11
- 3500-Mn B-11
- 3500-Na B-11
- 3500-Pb B-11
- 3500-V B-11
- 3500-Zn B-11

Table 1B. Updated Standard Methods



- 4110 B-D-11
- 4140 B-2011
- 4500-B B-11
- 4500-Cl⁻ B-G-11
- 4500-CN⁻ B-G-11
- 4500-F⁻ B-E-11
- 4500-H⁺ B-11
- 4500-NH₃ B-H-11
- 4500-NO²⁻ B-11
- 4500-NO₃⁻ D-F, H-11
- 4500-Norg B-D-11
- 4500-O B-G-11
- 4500-P B, E-H-11
- 4500-S₂ B-D, F, G-11
- 4500 SiO₂-C, E, F-11
- 5210 B-11
- 5220 B-D-11
- 5310 B-D-11
- 5520 B, F-11
- 5530 B, D-10
- 5540 C-11

Revised ASTM Methods



- D 511 – 09 (A, B)
- D 516 – 11
- D 858 – 12 (A – C)
- D 859 – 10
- D 1067 – 11
- D 1068 – 10 (A-C)
- D 1126 – 12
- D 1179 – 10 (A, B)
- D 1246 – 10
- D 1688 -12 (A - C)
- D 1691 – 12 (A, B)
- D 1976 – 12
- D 3223 -12
- D 3373 – 12
- D 3557 – 12 (A – D)
- D 4382 – 12
- D 4658 – 09
- D 5257 – 11
- D 5673 – 10
- D 5907 – 13
- D 6508 – 10
- D 7284 – 13
- D 7511 – 12

Other New Methods



- USGS Methods I-2547-11 and I-2548-11, *Colorimetric Determination of Nitrate Plus Nitrite in Water by Enzymatic Reduction, Automated Discrete Analyzer Methods*, for nitrate, nitrite, and combined nitrate-nitrite. I-2548-11 is a low level version of I- 2547-11.
- NECi Method N07-0003, *Method for Nitrate Reductase Nitrate-Nitrogen Analysis*;
- Timberline Instruments, LLC Method Ammonia- 001, *Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Conductivity Cell Analysis*;
- NCASI Method TNTP-W10900, *Total (Kjeldahl) Nitrogen and Total Phosphorus in Pulp and Paper Biologically Treated Effluent by Alkaline Persulfate Digestion*;
- Hach Company Method 10242, *Simplified Spectrophotometric Measurement of Total Kjeldahl Nitrogen in Water and Wastewater*;
- Hach Company Method 10206, *Spectrophotometric Measurement of Nitrate in Water and Wastewater*.

New and Revised Footnotes



52. Adds 1999 errata sheet to Method 300.1, cover sheet is not on EPA methods page, but can be found by searching.*

- Errata 1: Clarifying analyst role in meeting criteria when modifying methods
- Errata 2: Correct typo LRB to LFB
- Errata 3: Clarifying reporting data qualifiers for failed QC

78. Color - The pH adjusted sample is to be adjusted to 7.6 for NPDES reporting purposes.

Many trivial editorial corrections

Addition of references for sources of new methods

* Not discussed in the preamble

Other Changes to Table 1B



- Revise hardness entry to state “Ca plus Mg as their carbonates, by any approved method for Ca and Mg (See Parameters 13 and 33), provided that the sum of the lowest point of quantitation for Ca and Mg is below the NPDES permit requirement for Hardness
- Delete Method 200.5, for cobalt, molybdenum and thallium
- Moved methods around for Color
- Moved a CIE/UV method from ASTM to Other

Accredited labs



- 200.5 9
- 200.7 228
- 200.8 218
- 611 0
- 624 184
- 625 175

Out of 1429 labs in
LAMS

Table 1 C: Organics



New Methods

- 608.3 Pesticides and PCBs
- 624.1 Volatile Organics
- 625.1 Semivolatile Organics

Updated Methods

- SM 6200B-11, 6200C-11, 6440B-05
- ASTM D 7065 – 11

Revised Method

- 611 Haloethers (same name change as below)

Name change (Footnote 12)

- 2,2'-oxybis(1-chloropropane) was formerly inaccurately labeled as 2,2'-oxybis(2-chloropropane) and bis(2-chloroisopropyl) ether. Some versions of Methods 611, and 1625 inaccurately list the analyte as “bis(2-chloroisopropyl)ether,” but use the correct CAS number of 108-60-1.

Table 1D: Pesticides



- 1978 TLC methods still approved for 16 obscure pesticides
- 608, 624, 625 changed to 608.3, 624.1, 625.1

Updated Methods

- SM 6630B, C-07; 6440B-06

Table 1F: Pharmaceuticals



- 624 changed to 624.1

Table 1G: Pesticide Active Ingredients



- 608, 624, 625 changed to 608.3, 624.1, 625.1
- Added note 4: Permethrin is not listed within methods 608.3 and 625.1; however, cis-permethrin and trans-permethrin are listed. Permethrin can be calculated by adding the results of cis and trans-permethrin. *

* Not discussed in the preamble

Holding Times and Sample Preservation



- *E. Coli* and *Enterococcus*
 - Preservation changed from 0.0008% $\text{Na}_2\text{S}_2\text{O}_3$ to 0.008% $\text{Na}_2\text{S}_2\text{O}_3$
 - Add holding times for total/fecal coliforms, and fecal streptococci in Table IH.
- Cyanide and Microbiological
 - Footnotes 5 revised to clarify that treatment options for samples containing oxidants is specifically for cyanide analysis, and that the dechlorination procedures are specifically for microbiological analyses.

Alternate Test Procedures



- **136.4: Nationwide**
- Removed “permitting authority”
- Clarify the process for nationwide approval and the Regional ATP Coordinator’s role in limited use ATP approvals

- **136.5: Limited**
- Removed “permitting authority”
- Clarify the process for nationwide approval and the Regional ATP Coordinator’s role in limited use ATP approvals

The effect of the inadvertent change was to allow *State* permitting authorities to approve ATPs for limited use within the State. EPA never intended this

Method Modifications: 136.6



- New language on using vendor methods
 - Where the laboratory is using a vendor-supplied method, it is the QC criteria in the reference method, not the vendor's method that must be met to show equivalency. Where a sample preparation step is required (*i.e.*, digestion, distillation), QC tests are to be run using standards treated in the same way as samples.

Approval for nationwide use requires a rulemaking process. In the interim, a facility may apply to an EPA Region for a limited-use ATP approval letter, *i.e.* for use at that facility. Generally it is not necessary for the limited-use ATP applicant to submit data, or do a side-by-side comparison, if the method has already been reviewed for nationwide use under the CWA ATP program which requires multi-lab and comparability data and the review has resulted in a recommendation for inclusion in Part 136.

Method Modifications: 136.6



- Added new section on Notification*
 - The permittee must notify their permitting authority of the intent to use a modified method. Such notification should be of the form “Method xxx has been modified within the flexibility allowed in 40 CFR 136.6.” The permittee may indicate the specific paragraph of 136.6 allowing the method modification. Specific details of the modification need not be provided, but must be documented in the SOP and maintained by the analytical laboratory that performs the analysis.

* Not discussed in the preamble

Summary of Proposed Changes to Part 136



- Update many methods to current versions
- Correct technical errors
- Provide additional clarification

Changes to Appendix A



New Methods

- 608.3 Pesticides and PCBs
- 624.1 Volatile Organics
- 625.1 Semivolatile Organics

600 Series Methods



- Developed in the 1970s and reflected the best practice at the time, e.g.
 - Analytes = priority pollutants
 - Liquid-liquid extraction
 - Packed columns
 - Separate base/neutral and acid fractions because of special column needed for phenols
 - 3-point calibration
- Methods were inter-laboratory validated

Since 1979



- Other EPA Programs used these methods as a basis
 - Contract Laboratory Program SOWs
 - Drinking Water: 508, 524, 525
 - SW-846: 8080, 8081, 8082, 8240, 8250, 8260, 8270
- Expanded analyte lists
- New technology
 - Capillary columns
 - Solid Phase Extraction (SPE)
 - Selected Ion Monitoring (SIM)
 - Hydrogen carrier gas
- Additional QC

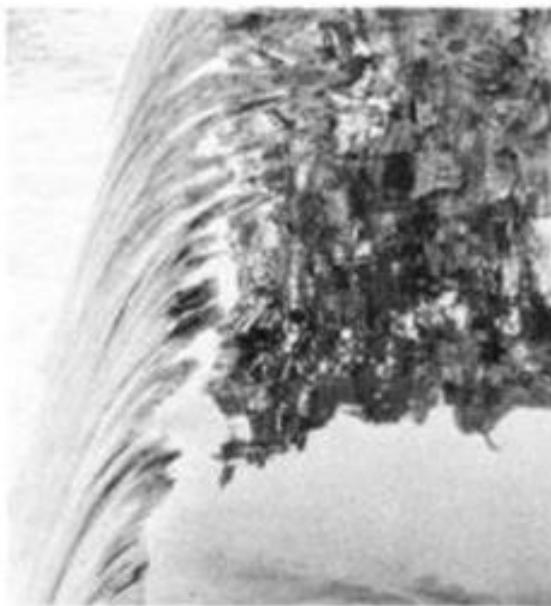
Trace analyses for wastewaters

Method detection limit, a new performance criterion for chemical analysis, is defined as that concentration of the analyte that can be detected at a specific confidence level. Both theory and applications are discussed for reliable wastewater analyses of priority pollutants

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The development of trace analysis methodology brought with it a series of questions about method performance at low concentration levels of analyte (1, 2, 3). Under Section 304(h) of the Clean Water Act, as amended in 1977, (4) the Environmental Monitoring and Support Laboratory (EMSL) in Cin-



ority pollutants, it was incumbent on EMSL to develop method perfor-

detection limit should be related to the standard deviation of the measured values at or near zero concentration of the analyte (11).

There is no doubt that the detection limit is one of the most important performance characteristics of an analytical procedure. In most cases, a detection limit must be viewed as a temporary limit to current methodology.

Complete analytical system

Ostensibly, analysts do not directly observe concentrations of analyte. The measurements of the transducer signal, which are related to the analyte concentration, are actually observed. In any analytical system, information concerning the identification and quantity of

Developments Since 1983



- 1984 MDL is promulgated in 40 CFR Part 136, Appendix B for use in the wastewater program and defined as 3.14 times the standard deviation of seven low level spiked blanks.
- Twenty-six years of controversy culminating in a FACDQ report
- 2010 TNI Chemistry committee begins work on a MDL revision and submits to EPA in 2014
- 2016 **EPA publishes revised MDL as part of the Methods Update Rule**

SUMMARY



- Not as dramatic as the 2010 rule
 - Most of this just adds new methods, corrects problems and increases flexibility
- New 600 Methods a great improvement from a technology perspective
- MDL is a incredible improvement!
- MDL is completely consistent with the new TNI standard!

Implementation Options



Rule will be effective 30 days after publication!

- Do nothing.
- 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.
- The new MDL procedure is also published on the TNI website and referenced in the 2016 TNI laboratory standard.

Feel Free to Write EPA



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